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EPA METHOD STUDY 25,
METHOD 602, PURGEABLE AROMATICS

by

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16. ABSTRACT

The experimental design and the results of an interlaboratory study for an analytical method to detect purgeable aromatics in water are described herein. The method, EPA Method 602, Purgeable Aromatics, employs a purge-and-trap chromatographic technique for determination of seven aromatic hydrocarbon analytes in water matrices. The three Youden pairs of spiking solutions used in this study contained benzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, ethylbenzene and toluene. The six water types used in the study were distilled water, drinking water, surface water, and three wastewater samples from industries employing or producing aromatic hydrocarbons. Twenty laboratories participated in the Method 602 validation study. The participating laboratories supplied their individual distilled, drinking, and surface water samples. Monsanto Research Corporation (MRC) supplied the three industrial wastewater samples. The statistical analyses and conclusions reached in this report are based on the analytical data obtained by the 20 participating laboratories.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati research responsibilities are to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication reports the results of EPA's interlaboratory method study for the following compounds:

benzene
chlorobenzene
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
ethylbenzene
toluene

Federal agencies, states, municipalities, universities, private laboratories, and industry should find this interlaboratory study useful in monitoring and controlling pollution in the environment.

Robert L. Booth, Acting Director
Environmental Monitoring and Support Laboratory

ABSTRACT

Described herein are the experimental design and the results of an interlaboratory study of an analytical method for detecting purgeable aromatics in water. The method, EPA Method 602, Purgeable Aromatics, employs a purge-and-trap chromatographic technique for determining seven aromatic hydrocarbon analytes in water matrices. Three Youden pairs of spiking solutions were used and contained benzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, ethylbenzene, and toluene. Six water types were used: distilled water, drinking water, surface water, and three wastewater samples from industries employing or producing aromatic hydrocarbons. Twenty laboratories participated and supplied their individual distilled, drinking, and surface water samples. Monsanto Company supplied the three industrial wastewater samples. The statistical analyses and conclusions reached in this report are based on the analytical data obtained by the 20 participating laboratories.

Participating laboratories were selected based upon technical evaluation of proposals and upon the analytical results of prestudy samples. The data obtained from the interlaboratory study were analyzed employing a series of computer programs known as the Interlaboratory Method Validation Study (IMVS) system, which was designed to implement the concepts recommended in ASTM Procedure D 2777. The statistical analyses included tests for the rejection of outliers, estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

This report was submitted in fulfillment of Contract 68-03-2856 by Monsanto Company under the sponsorship of the U.S. Environmental Protection Agency and covers a period from September 1979 to December 1982.

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SECTION 1

INTRODUCTION

The various analytical laboratories of the U.S. Environmental Protection Agency (EPA) gather water quality data to provide information on water resources, to assist research activities, and to evaluate pollution abatement activities. The success of the Agency's pollution control activities, particularly when legal action is involved, depends upon the reliability of the data provided by the laboratories.

Under provisions of the Clean Water Act, the EPA is required to promulgate guidelines establishing test procedures for the analysis of pollutants. The Clean Water Act Amendments of 1977 emphasize the control of toxic pollutants and declare the 65 "priority" pollutants and classes of pollutants to be toxic under Section 307(a) of the Act. This report is one of a series that investigates the analytical behavior of selected priority pollutants and suggests a suitable test procedure for their measurement. The priority pollutants to be analyzed by Method 602 covered by this report are the following purgeable aromatics:

benzene
chlorobenzene
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
ethylbenzene
toluene

The Environmental Monitoring and Support Laboratory-Cincinnati (EMSL-Ci) of the EPA develops analytical methods and conducts a quality assurance program for the water laboratories. This program is designed to maximize the reliability and legal defensibility of all water quality information collected by EPA laboratories. The responsibility for these activities is assigned to the Quality Assurance Branch (QAB). One of these activities is to conduct interlaboratory tests of the methods. This report presents the results of interlaboratory study 25 on Method 602 for purgeable aromatics.

The study consisted of three distinct phases. Phase I involved the analysis of the prestudy samples by 20 participating laboratories. Two samples were analyzed for each of the seven purgeable aromatics; a medium concentration sample to be analyzed in drinking water supplied by the participating laboratories and a low level sample to be analyzed in a wastewater sample supplied by Monsanto Company. The objective of Phase I was to become familiar with the methodology employed and to identify any potential problems associated with the analytical methodology. Accuracy was not as important as being familiar with the methodology. A short report, including the data obtained and any potential problems encountered, was received by Monsanto Company at the completion of Phase I from each subcontracting laboratory.

Phase II consisted of a prestudy conference held at U.S. Environmental Protection Agency (EPA) in Cincinnati, Ohio, after the data from the Phase I samples had been evaluated. The purpose of the prestudy conference was to discuss the results of the Phase I sample analyses and any problems encountered in the methodology. Each subcontracting laboratory sent at least one analyst to this meeting.

Phase III consisted of the formal interlaboratory study. Each of the seven aromatic purgeables were analyzed at six concentrations (three Youden pairs) in six different water matrices. The participating laboratories each supplied its own distilled water, drinking water and surface water. Monsanto Company supplied the three industrial wastewaters. In addition, the participating laboratories performed analyses of all water blanks with no spiked compounds. Each participating laboratory then issued a report to Monsanto Company containing all data obtained, copies of all chromatograms, and any comments.

The final step in the study was to conduct a statistical analysis of all data obtained. This analysis was conducted by Battelle Columbus Laboratories, Columbus, Ohio, under contract 68-03-2624 employing a system of computer programs known as the Interlaboratory Method Validation Study (IMVS) system.

SECTION 2

CONCLUSIONS

The object of this study was to characterize the performance of Method 602 in terms of accuracy, overall precision, single-analyst precision and the effect of water types on accuracy and precision. Through statistical analyses of 5,040 analytical values, estimates of accuracy and precision were made and expressed as regression equations, which are shown in Table 1.

The accuracy of the method is obtained by comparing the mean recovery to the true values of the concentration. Expressed as percent recovery it ranges from 88% to 97% in distilled, tap, and surface water. Excluding the values where large interferences entered into play, the accuracy in wastewaters ranges from 84% to 100%. Large interferences (background) existed in wastewater 5 for chlorobenzene and toluene. At the lowest concentration levels, recoveries exceeding 500% were reported. At the middle and high levels, average recoveries were 94% and 86%, respectively, for chlorobenzene and toluene.

The overall standard deviation indicates the precision associated with measurements generated by a group of laboratories. The percent relative standard deviation (%RSD) for all waters, ranges from 9.9% to 39.8% for the middle and high Youden pairs. The low Youden pair ranges from 20.9% to 55% in distilled, tap, and surface water. The range in wastewater is 30.5% to 63.7% excluding chlorobenzene and toluene. In all cases, the highest %RSD (poorest precision) was at the lowest Youden pair.

TABLE 1. REGRESSION EQUATIONS FOR ACCURACY AND PRECISION

WATER TYPE	BENZENE	CHLOROBENZENE	1,2-DICHLOROBENZENE	1,3-DICHLOROBENZENE
APPLICABLE CONC. RANGE	(2.20 - 550.00)	(2.20 - 551.00)	(2.20 - 600.00)	(2.20 - 550.00)
DISTILLED WATER				
SINGLE-ANALYST PRECISION	SR = 0.09X + 0.59	SR = 0.09X + 0.23	SR = 0.17X - 0.04	SR = 0.15X - 0.10
OVERALL PRECISION	S = 0.21X + 0.56	S = 0.17X + 0.10	S = 0.22X + 0.53	S = 0.19X + 0.09
ACCURACY	X = 0.92C + 0.57	X = 0.95C + 0.02	X = 0.93C + 0.52	X = 0.96C - 0.05
TAP WATER				
SINGLE-ANALYST PRECISION	SR = 0.11X - 0.06	SR = 0.10X + 0.12	SR = 0.10X + 0.42	SR = 0.08X + 0.33
OVERALL PRECISION	S = 0.22X + 1.11	S = 0.16X + 0.36	S = 0.18X + 0.28	S = 0.15X + 0.33
ACCURACY	X = 0.97C + 0.85	X = 0.94C + 0.12	X = 0.91C + 0.44	X = 0.93C + 0.21
SURFACE WATER				
SINGLE-ANALYST PRECISION	SR = 0.08X + 0.17	SR = 0.08X + 0.14	SR = 0.10X + 0.04	SR = 0.10X + 0.01
OVERALL PRECISION	S = 0.19X + 0.38	S = 0.19X + 0.20	S = 0.18X + 0.12	S = 0.18X + 0.80
ACCURACY	X = 0.93C + 0.37	X = 0.92C - 0.14	X = 0.89C + 0.21	X = 0.93C + 0.40
WASTE WATER 1				
SINGLE-ANALYST PRECISION	SR = 0.13X + 0.56	SR = 0.08X + 3.02	SR = 0.11X + 0.93	SR = 0.15X + 0.46
OVERALL PRECISION	S = 0.26X + 0.69	S = 0.21X + 2.33	S = 0.25X + 0.37	S = 0.36X + 0.83
ACCURACY	X = 0.91C + 0.06	X = 0.93C + 1.85	X = 0.90C + 0.38	X = 1.00C + 3.36
WASTE WATER 2				
SINGLE-ANALYST PRECISION	SR = 0.09X + 0.89	SR = 0.09X +14.83	SR = 0.10X + 0.90	SR = 0.10X + 0.52
OVERALL PRECISION	S = 0.25X + 0.97	S = 0.31X +11.81	S = 0.17X + 1.12	S = 0.19X + 0.79
ACCURACY	X = 0.87C + 0.36	X = 0.63C +19.77	X = 0.95C + 0.69	X = 0.92C + 0.50
WASTE WATER 3				
SINGLE-ANALYST PRECISION	SR = 0.10X + 0.43	SR = 0.10X + 0.43	SR = 0.15X + 0.14	SR = 0.12X + 0.29
OVERALL PRECISION	S = 0.25X + 0.58	S = 0.16X + 0.85	S = 0.18X + 0.51	S = 0.16X + 0.43
ACCURACY	X = 0.93C + 0.50	X = 0.92C + 0.15	X = 0.88C - 0.39	X = 0.94C + 0.16

X = MEAN RECOVERY
C = TRUE VALUE FOR THE CONCENTRATION

TABLE 1 (continued)

WATER TYPE	1,4-DICHLOROBENZENE	ETHYLBENZENE	TOLUENE
APPLICABLE CONC. RANGE	(2.20 - 550.00)	(2.20 - 551.00)	(2.10 - 550.00)
DISTILLED WATER			
SINGLE-ANALYST PRECISION	SR = 0.15X + 0.28	SR = 0.17X + 0.46	SR = 0.09X + 0.48
OVERALL PRECISION	S = 0.20X + 0.41	S = 0.26X + 0.23	S = 0.18X + 0.71
ACCURACY	X = 0.93C - 0.09	X = 0.94C + 0.31	X = 0.94C + 0.65
TAP WATER			
SINGLE-ANALYST PRECISION	SR = 0.09X + 0.39	SR = 0.10X + 0.18	SR = 0.10X + 0.18
OVERALL PRECISION	S = 0.15X + 0.39	S = 0.20X + 0.68	S = 0.21X + 0.16
ACCURACY	X = 0.91C + 0.26	X = 0.97C + 0.41	X = 0.94C + 0.17
SURFACE WATER			
SINGLE-ANALYST PRECISION	SR = 0.12X - 0.06	SR = 0.08X + 0.33	SR = 0.08X + 0.18
OVERALL PRECISION	S = 0.17X + 0.85	S = 0.21X + 0.36	S = 0.25X + 0.33
ACCURACY	X = 0.88C + 0.27	X = 0.93C + 0.20	X = 0.93C + 0.02
WASTE WATER 1			
SINGLE-ANALYST PRECISION	SR = 0.07X + 0.85	SR = 0.12X + 0.38	SR = 0.11X + 1.05
OVERALL PRECISION	S = 0.18X + 0.59	S = 0.21X + 0.40	S = 0.24X + 0.67
ACCURACY	X = 0.89C + 0.54	X = 0.94C + 0.38	X = 0.87C + 0.99
WASTE WATER 2			
SINGLE-ANALYST PRECISION	SR = 0.10X + 0.85	SR = 0.11X + 0.45	SR = 0.18X + 3.47
OVERALL PRECISION	S = 0.19X + 0.49	S = 0.25X + 0.53	S = 0.28X + 4.36
ACCURACY	X = 0.95C + 0.33	X = 0.86C + 0.14	X = 0.71C + 8.63
WASTE WATER 3			
SINGLE-ANALYST PRECISION	SR = 0.09X + 0.34	SR = 0.13X + 0.52	SR = 0.10X + 1.20
OVERALL PRECISION	S = 0.15X + 0.33	S = 0.20X + 0.78	S = 0.21X + 1.55
ACCURACY	X = 0.91C + 0.11	X = 0.89C + 0.73	X = 0.91C + 1.01

X = MEAN RECOVERY
C = TRUE VALUE FOR THE CONCENTRATION

The single-analyst standard deviation indicates the precision associated within a single laboratory. The percent relative standard deviation for a single analyst (%RSD-SA) for all waters, ranges from 6.1% to 31.8% for the middle and high Youden pair. The low Youden pair ranges from 9.0% to 33.7% for distilled, tap, and surface water. The range in wastewaters is 20.9% to 43.5%, excluding chlorobenzene and toluene. In all cases, the highest %RSD-SA (poorest precision) was at the lowest Youden pair.

A statistical comparison of the effect of water type was performed indicating a statistically significant difference for six of the analyte/water matrix combinations. Of these six cases, a practical significant difference was established in only two cases; chlorobenzene and toluene in water 5.

SECTION 3

RECOMMENDATIONS

Method 602 is recommended for the analysis of purgeable aromatics in municipal and industrial wastewaters. The accuracy and precision are acceptable, while the matrix effects are significant only at low concentration levels.

Because deposition of high-boiling compounds and column bleed onto the photoionization detector (PID) lamp window causes a continual loss of detector response, frequent cleaning of the lamp window is recommended. This may be aleviated by not exceeding the column temperature 90°C recommended in Method 602. Venting of the column at higher temperature (e.g., 150°C) through the detector can lead to fouling of the detector window.

Potential carry-over problems from contaminated water can be lessened or eliminated by analyzing a blank sample prior to the next water sample.

Care must be taken in the preparation of laboratory pure water. Contamination from solvents in the atmosphere is common.

Teflon is not recommended for gas lines. Methylene chloride permeates the Teflon, and naphthalene, which is used as a lubricant in the drawing of the Teflon, responds to the PID. Copper or stainless steel gas lines are recommended.

SECTION 4

DESCRIPTION OF STUDY

SELECTION OF PARTICIPATING LABORATORIES

In June 1980, as prime contractor, Monsanto Company sent requests for quotation (RFQ) to approximately 150 laboratories which had been identified as potential subcontractors for this interlaboratory study. The RFQ contained a Scope of Work, the fixed price allowed for the effort, a description of the projected timing of the required analyses, and a copy of the analytical method. The detailed writeup for Method 602 as published by EPA on 15 May 1979 is presented in Appendix A of this report. Interested laboratories were asked to respond to the RFQ by providing the following information:

- Facilities available at the laboratory, including all instrumentation to be used for the study.
- Previous experience in carrying out the types of analyses specified in the Scope of Work for the compounds of interest.
- Handling procedures for working with hazardous and potentially hazardous chemicals.
- The organization and managerial structure of the laboratory, identifying those personnel involved in managing this study.

- The analyst involved in the analyses to be performed, including his/her experience.

- Quality control/quality assurance procedures and good laboratory practices followed by the laboratory.

Approximately 25 proposals were received in response to the RFQ. The proposals received were ranked, and the 20 most qualified laboratories were selected for participation. Table 2 lists the participating laboratories for the EPA Method 602 interlaboratory study. Throughout this report, data provided by these laboratories will be identified only by an anonymous code number.

Phase I - Analysis of Prestudy Conference Samples

In November 1980, MRC forwarded to each of the 20 participating laboratories two sealed glass ampuls containing mixed concentrates of the seven aromatic compounds in methanol, and a sample of an industrial wastewater. Also forwarded were procedures for the preparation of stock solutions, procedures for the preparation of aqueous calibration standards, and procedures for spiking the drinking water and wastewater with the prestudy samples contained in the ampuls. The recommended procedures are presented in Tables 3, 4, and 5.

At this same time, applicable notes on Method 602 were sent to each participating laboratory. The notes on Method 602 for the analysis of preconference samples are included in Appendix B of this report and referenced by paragraph/section number of the test method as presented in Appendix A. The notes on Method 602 included recommended procedures to minimize cross contamination from sample to sample, recommended procedures for cleaning the purge path and analytical column of high-boiling compounds, appropriate purge/trap samplers and purging vessel design and capacities, recommended contents of the sorbent trap, methods to

TABLE 2. LABORATORIES PARTICIPATING IN EPA METHOD 602 INTERLABORATORY STUDY

Acurex Corporation
285 Clyde Avenue
Mountain View, CA 94042

Analytics
Division of CBL
Subsidiary of Rohm & Haas Co.
1415 Rhoadmiller
Richmond, VA 23260

Clayton Environmental Consultants, Inc.
25711 Southfield Road
Southfield, MI

Engineering Science, Inc.
Research and Development Laboratory
600 Bancroft Way
Berkeley, CA 94710

Environmental Research Group, Inc.
117 North First
Ann Arbor, MI 48104

ERCO/Energy Research Co., Inc.
185 Alewife Brook Parkway
Cambridge, MA 02138

Global Geochemistry Corp.
6919 Eton Avenue
Canoga Park, CA 91303

Jacobs Laboratories (formerly PJB
Laboratories)
373 South Fair Oaks Avenue
Pasadena, CA 91105

Normandeau Associates, Inc. (formerly
Texas Instruments, Inc.)
1710 Firman Drive
Richardson, TX 75081

Northrop Services, Inc.
Environmental Services
P.O. Box 437
Little Rock, AR 72203

O'Brien & Gere Engrs., Inc.
Box 4873
1304 Buckley Road
Syracuse, NY 13221

Orlando Laboratories, Inc.
P.O. Box 8008
90 West Jersey Street
Orland, FL 32806

PEDCo Environmental, Inc.
11499 Chester Road
Cincinnati, OH 45246

SERCO Laboratories
Sanitary Engineering Laboratories, Inc.
1931 West County Road, C2
Roseville, MN 55113

State of New York
Department of Health
Tower Building
The Governor Nelson A. Rockeller
Empire State Plaza
Albany, NY 12201

Technical Services, Inc.
103-7 Stockton Street
P.O. Box 52329
Jacksonville, FL 32201

UBTL, Division of University of Utah
Research Institute
520 Wakara Way
Salt Lake City, UT 84108

Versar, Inc.
6621 Electronic Drive
Springfield, VA 22151

Weston Designers Consultants
Weston Way
West Chester, PA 19380

Wilson Laboratories
Analytical & Research Chemists and
Biologists
528 North Ninth
Salina, KS 67401

TABLE 3. PROCEDURE FOR PREPARATION OF STOCK SOLUTIONS

1. Place about 9.8 mL of methyl alcohol into a ground glass stoppered 10-mL volumetric flask.

2. Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces have dried.

3. Weigh the flask to the nearest 0.1 mg.

4. Using a 100-µL syringe, immediately add 2 drops of the reference standard to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5. Dilute to volume, stopper, then mix by inverting the flask several times.

6. Transfer the solution to a dated and labeled 15-mL screw-cap bottle with a Teflon® cap liner.

7. Calculate the concentration in micrograms per microliter from the net gain in weight.

8. Store the solution at 4°C.

   All standard solutions prepared in methyl alcohol are stable up to four weeks when stored under these conditions. They should be discarded after that time has elapsed.

   Because of the toxicity of the purgeables, it is necessary to prepare primary dilutions in a hood. It is further recommended that a NIOSH/MESA-approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

TABLE 4. PROCEDURE FOR PREPARATION OF AQUEOUS CALIBRATION STANDARDS

To prepare accurate standard solutions, the following precautions must be observed:

- Do not inject less than 20 μL of alcoholic standards into 100 mL of reagent water.
- Use a 25-μL Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standard into water.)
- Rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.
- Mix aqueous standards by inverting the flask three times only.
- Never use pipets to dilute or transfer samples or aqueous standards.
- Aqueous standards when stored with a headspace are not stable and should be discarded after one hour.

TABLE 5. PROCEDURE FOR SPIKING WATER

If duplicate analyses are to be performed on one ampul, concurrently perform all of the following steps below in duplicate:

- Fill a 100-mL volumetric flask to volume with reagent water.
- Stablize the ampuls to 20°C.
- Use a 25-µL Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standard into water.)
- Open the ampuls by breaking off the top at the break area on the neck and immediately fill the syringe.
- Rapidly inject 20 µL of the ampul concentrate into the expanded area of the filled volumetric flask. Remove the needle as fast as possible after injection.
- Mix the sample by inverting the flask three times only.
- Never use pipets to dilute or transfer samples or aqueous standards.
- Aqueous solutions when stored with a headspace are not stable and should be discarded after one hour.

control loss in the PID (especially in the analyses of wastewater matrices), recommended purge, desorb and vent cycles, recommended use of organic-free water to prevent contamination from laboratory air, and recommended quality assurance practices.

The notes on Method 602 were developed after agreement was reached by EPA and MRC concerning which method steps were to be rigidly fixed and which conditions could be optimized by the individual laboratory. Some latitude was permitted in (1) selection of purge/trap samples (Hewlett-Packard as well as Tekmar); (2) trap material (potential omission of 3% OV-1); (3) chromatographic column material either 5% SP-1200 or 5% SP-2100. The majority of the Method 602 procedural steps were to be rigidly observed in this interlaboratory study.

Notes on Method 602 largely resulting from the experience gained by MRC analysts in the preliminary studies of the method are presented in Appendix C.

The two ampuls sent to the participating laboratories for the prestudy conference analyses contained concentrated mixtures of the seven aromatic compounds such that, when they were spiked into the two waters, the resulting concentrations of the individual aromatics would be:

Ampul	Concentration
1	50 to 63 μg/L
2	2.5 to 3.2 μg/L

The analysis of the higher concentration sample in drinking water assured that the method could be properly implemented by the laboratories with a minimum of difficulty. Analysis of the lower concentration in the wastewater was intended to evaluate any method or detection limit problems that could arise under more adverse conditions. The results of these analyses are presented in Table 6.

TABLE 6. RESULTS OF METHOD 602 PRESTUDY ANALYSES: PURGEABLE AROMATICS (μg/L)

Laboratory	Compound													
	Benzene		Chlorobenzene		1,2-Dichlorobenzene		1,3-Dichlorobenzene		1,4-Dichlorobenzene		Ethylbenzene		Toluene	
01	44	ND	38	ND	44	ND	44	ND	44	ND	44	ND	42	ND
02	52.6	1.1	42.3	1.0	55.6	1.1	53.7	1.0	57.2	0.1	54	1.2	53.4	ND
03	49	2.3	64	11	59	2.1	61	1.5	56	0.3	57	1.4	46	120
04	34.66	0.48	43.63	0.64	34.56	0.42	34.33	0.64	36.88	ND	41.77	1.07	40.00	70.89
05	42	0.5	38	6	46	2.2	51	1.6	40	ND	49	1.4	45	128
06	4.46	0.05	4.57	0.14	5.00	0.11	5.52	0.08	6.13	0.01	6.67	0.08	5.71	1.79
07	50.5	0.954	40.7	1.68	48.9	1.573	51.8	0.14	52.9	0.192	48.5	1.094	51.1	ND
08	58	1	38	4	64	5	56	4	66	<1	44	<1	48	120
09	49	2.8	53	1.6	67	0.8	63	2.1	63	0.3	78	1.2	67	12
10	61	ND	45	7.1	26	1.5	54	1.2	55	0.4	59	1.1	60	115
11	3.8	0.5	2.1	0.6	ND	ND	2.3	2.0	1.6	1.8	2.6	0.2	2.6	9.9
12	ND	ND	32	6.3	48	2.9	47	2.5	45	1.3	46	2.6	45	126
13	87.2	ND	54.3	ND	68.5	ND	61.1	ND	59.7	ND	62.5	ND	88.0	ND
14														
15														
16														
17	40	ND	9.5	55.2	45.0	3.3	40.2	3.0	48.5	1.0	11.3	12.5	44	100.1
18														
19														
20														
True value	50	2.5	63	3.2	50	2.5	50	2.5	51	2.6	50	2.5	50	2.5
Mean[a]	41	0.7	36	6.8	44	1.5	45	1.4	45	0.5	43	1.8	46	57
Standard deviation	24	0.9	19	14	21	1.5	19	1.2	19	0.6	22	3.2	22	58
Range	ND-87.2	ND-2.8	2.1-64	ND-55.2	ND-68.5	ND-5	2.3-63	ND-4	1.6-66	ND-1.8	2.6-78	ND-12.5	2.6-88	ND-128

[a] Data reported as "Not Detected" was calculated as 0. Data reported as $<X_i$ was calculated as X_i.

The data shown in Table 6 include correction for the blank values of the aromatics in the various laboratories' drinking water and in the wastewater. If the value for a compound in the blank was greater than or equal to the value in the sample, ND (not detected) was reported. N-1 statistics were used to calculate the standard deviation; ND was calculated as "0", $<X_i$ was calculated as "X_i", and NA (not analyzed) was ignored in the calculations. The "true value" listed for each individual compound is the calculated value of the final concentration in the drinking water after adding the prescribed 20-µL volume of the concentrated spiking solution (delivered in sealed ampuls) to the prescribed 100-mL volume of drinking water.

Phase II - Prestudy Conference

After the participating laboratories analyzed the prestudy conference samples, the analysts from the 20 laboratories met in Cincinnati, Ohio on 15 January 1981, discussed the EPA Method 602 procedure, and identified the following potential problems:

- Some subcontractors reported difficulties in achieving the stated detection limits. The detection limits given for Method 602 were determined in distilled water. Higher detection limits could be expected for other waters types.

- Several laboratories observed the loss of sensitivity for the PID due to contamination of the MgF_2 PID window. The PID window must be cleaned frequently when running a large number of samples. The frequency of cleaning will depend on the number of samples analyzed over a period of time and the relative level of contamination in the samples. [Note: EPA in-house experience is that when Method 602 (Appendix A) is used exactely as proposed, the HNU high temperature Model PI-51 detector is stable for extended periods of time, i.e., 6 weeks. If the low temperature model detector is substituted or if the column is heated above 90°C and purged through the detector, detector window fouling and subsequent instability can result.]

- A quenching effect of the PID is observed whenever water or methanol is eluting from the column.

- Poor separation of the given compounds may be due to the column. A poorly packed column, packing degradation, and improper packing material can cause poor resolution.

Phase III - Interlaboratory Method Study

The method study samples were sent to the participating laboratories in March 1981. The design of the interlaboratory method study was based on Youden's original plan for collaborative evaluation of precision and accuracy for analytical methods [1]. According to Youden's design, instead of duplicate analyses, samples are analyzed in pairs, and each sample of a pair has slightly different concentrations of the constituents. The analyst is directed to perform a single analysis and report one value for each sample.

Six spiking solutions were made such that three different concentration ranges were each represented by two different solutions (a Youden pair). The spiking solutions, which were sent in sealed ampuls, were at such a concentration that after dilution in water, solutions 1 and 2 would have aromatic concentrations at a low level of about 2 μg/L, solutions 3 and 4 would have concentrations at about 50 μg/L, and solutions 5 and 6 would yield concentrations about 10 times the intermediate level. Table 7 shows the individual aromatic compound concentrations that should result from each spiked water sample.

TABLE 7. CONCENTRATIONS OF AROMATICS IN SPIKED SOLUTIONS (µg/L)

Compound	Solution concentration					
	1	2	3	4	5	6
Benzene	2.2	3.0	46	54	450	550
Chlorobenzene	2.2	3.0	46	54	450	551
1,2-Dichlorobenzene	2.2	3.0	46	54	449	600
1,3-Dichlorobenzene	2.2	3.0	46	54	450	550
1,4-Dichlorobenzene	2.2	3.0	46	54	450	550
Ethylbenzene	2.2	3.0	46	54	452	551
Toluene	2.1	3.0	46	54	450	550

The concentrated spiking solutions shipped to the participating laboratories were sealed in glass ampuls employing a Cozzoli Model HS1 ampul sealer. Analyses of the concentrations of the aromatic compounds in the ampuls shipped to the participating laboratories were conducted by MRC employing direct injection chromatographic procedures. These data are reported in Appendix D.

The participating laboratories again received instructions for the analysis of the aromatic compounds in the six water samples including the procedures for preparation of stock solutions, calibration standards, and quality control samples. In addition, each laboratory received a questionnaire and notes from the pre-study conference.

The results from the 20 participating laboratories employing EPA Method 602 for analysis of the seven aromatic compounds in the six water samples are presented in Appendix E. All values shown are corrected for blank values. Corrected values less than zero are shown as zero.

When informed that there might be some consistent error in their data, Laboratory 12 responded with a new set of data stating that data was originally quantitated using peak heights, and that a change in integrator attenuation was inadvertantly omitted from the earlier calculations. At that time, Monsanto Company could not substantiate this change in data values, and it was decided that the earlier data should be subjected to statistical analysis. The revised data from Laboratory 12 are presented in Appendix F of this report.

SECTION 5

STATISTICAL TREATMENT OF DATA

Data obtained from the interlaboratory study were subjected to statistical analyses by the Battelle Columbus Laboratories, Columbus, Ohio, under EPA Contract 68-03-2624. The analyses were performed employing the Interlaboratory Method Validation Study (IMVS) system [2] of computer programs. This system of programs was designed to implement ASTM procedure D2777, "Standard Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water" [3]. The analyses conducted using the IMVS system included tests for the rejection of outliers (both whole laboratories for a water type and individual data points), estimation of mean recovery (accuracy), estimation of single-analyst and overall precision, and tests for the effects of water type on accuracy and precision.

REJECTION OF OUTLIERS

An outlying observation, or "outlier," is a data point that appears to deviate markedly from other members of the sample in which it occurs. Outlying data points are very commonly encountered during interlaboratory test programs; if they are not removed, they can result in a distortion of the accuracy and precision statistics which characterize the analytical method. These outlying points cannot be removed indiscriminantly, however, because they may represent an extreme manifestation of the random variability inherent in the method.

ASTM procedure E178-80, "Standard Practice for Dealing with Outlying Observations" [4], and ASTM procedure D2777-77 [3] present explicit statistical rules and methods for identification of outliers.

Data from outlying laboratories for a particular water type were rejected employing Youden's laboratory ranking test procedure [3, 5] at the 5% level of significance. Data remaining after the laboratory ranking procedure were subjected to individual outlier tests. After all zero, missing, "less than" and "nondetect" data were rejected as outliers, the average and standard deviation for all remaining data were examined using one sided Student's t-test outlier rejection test constructed by Thompson [6]. All data rejected as outliers for this study are identified by an asterisk in the tables of raw data shown in Appendix E.

Youden's Laboratory Ranking Procedure

Using the data for each water type, Youden's laboratory ranking test [3, 5] was performed at the 5% level of significance. The Youden laboratory ranking procedure requires a complete set of data from each laboratory within each water type. Missing data from laboratory "i" for water type "j" were replaced by the following procedure. Letting X_{ijk} denote the reported measurement from laboratory "i" for water type "j" and concentration level C_k, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad (1)$$

where β_j and γ_j are fixed parameters which determine the effect of water type "j;" L_i is the systematic error due to laboratory "i," and ε_{ijk} is the random intralaboratory error.

Taking natural logarithms, it follows that

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \qquad (2)$$

which is a linear regression model with dependent variable $\ell n\, X_{ijk}$ and independent variable $\ell n\, C_k$. (Details and justification for this model are discussed in the section "Comparison of Accuracy and Precision Across Water Types.")

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for the six ampuls in each water type. The predicted values for $\ell n\hat{\ } X_{ijk}$ were obtained from the regression equation, and the missing values for X_{ijk} were estimated by $\hat{X}_{ijk} = \exp(\ell n\hat{\ } X_{ijk})$. (For complete details of this procedure, see Reference 2.)

An example of the use of Youden's laboratory ranking procedure is presented in Table 8, where the rankings of the values for benzene in water 3 are listed for each laboratory and for ampuls 1 through 6. For 20 laboratories and six ampuls, the upper and lower critical limits of the sums of the rankings are 104 and 22. If the sum of the rankings of any laboratory equals or exceeds 104, or is equal to or less than 22, that laboratory's data is rejected for all determinations for that analyte (benzene) in that water (water 3). From Table 8 it is apparent that the data from laboratories 15 and 16 must be rejected. In addition, the data from laboratory 12 was rejected because the non-detected value of ampul 1 skewed the cumulative score to exceed the lower limit of 22. The estimated missing data were then removed from the data sets.

Test for Individual Outliers

The data remaining after rejection of all zero, missing, "less than," and "nondetect" data were subjected to an individual outlier

TABLE 8. YOUDEN LABORATORY RANKING PROCEDURE FOR BENZENE DATA IN WATER 3

Laboratory number	Ranking values						Cumulative score
	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6	
1	8	16	17	18	18	18	95
2	4	5	11	12	6	5	43
3	15	18	20	20	3	3	79
4	9	11	9	8	8	7	52
5	13	15	16	16	11	9	80
6	7	13.5	15	13	16	16	70.5
7	10	10	12	11	9	11	63
8	18	19	8	15	5	10	75
9	3	4	5	7	20	20	59
10	12	13.5	7	4	12.5	6	55
11	16	7	10	17	14.5	15	79.5
12	20	9	1	1	1	1	33[a]
13	19	2	3	2	4	4	34
14	6	6	13	10	7	8	50
15	1	1	2	3	2	2	11[b]
16	17	20	19	19	19	12	106[b]
17	2	3	4	6	17	19	51
18	5	12	6	5	12.5	13	53.5
19	14	17	18	9	10	14	82
20	11	8	14	14	14.5	17	78.5

[a] Laboratory 12 rejected since ampul 1 value was a "nondetected" skewing rating to exceed lower (22) limit.

[b] Laboratories rejected versus upper and lower criteria of 104 and 22.

test based on calculation of the average value, $\bar{X}$, for each ampul and the standard deviation of the remaining values.

The criterion for rejection of individual outliers is based on calculation of Thompson's T-value [3,6].

In these calculations the mean recovery, $\bar{X}$, is given by

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \tag{3}$$

and the standard deviation, s, is given by

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2} \qquad (4)$$

where X_i = individual analyses
n = number of retained analyses values in the ampul set

The Thompson's T-test is defined as

$$T_i = \frac{X_e - \bar{x}}{s} \qquad (5)$$

where X_e is the retained X_i value farthest away from the mean ($\bar{X}$) of the set of retained data. The data point maybe rejected if the value of T calculated exceeds critical values for T (two-sided test 25% significance level) as presented in Table 9. If the extreme value is rejected as an outlier, the test is repeated for the next most extreme value among the remaining data until the value being tested passes the test. Table 10 summarizes calculations to examine suspect data points for benzene in water 3 by the T-test for outliers.

As shown in Table 10, six additional data points are identified as outliers by the Thompson T-test for the illustrative example of the analyte benzene in water 3. In summary, of the original 120 data points for benzene in water 3 (20 laboratories x 6 ampuls), all data points for laboratories 12, 15, and 16 were rejected on the basis of Youden's laboratory ranking procedure (total of 18 points), and seven additional data points were found to be outliers based on Thompson's T-test (for a total of the 25 data points). These same outlier tests were applied for all seven analytes in the six water matrices. All outlier data points are marked with an asterisk in Appendix E.

TABLE 9. CRITICAL VALUES FOR THOMPSON'S T (TWO-SIDED TEST) WHEN STANDARD DEVIATION IS CALCULATED FROM THE SAME SAMPLES

Number of observations, n	5% significance level
3	1.15
4	1.48
5	1.71
6	1.89
7	2.02
8	2.13
9	2.21
10	2.29
11	2.36
12	2.41
13	2.46
14	2.51
15	2.55
16	2.58
17	2.62
18	2.65
19	2.68
20	2.71

TABLE 10. RESULTS OF TEST FOR INDIVIDUAL OUTLIERS (BENZENE IN WATER 3)

Ampul	Laboratory	Extreme Value	Mean	deviation	Calculated T	Critical T	Decision
2	13	14.70	4.05	3.12	3.41	2.62	Reject
1	17	7.19	2.79	1.38	3.22	2.62	Reject
2	17	8.27	3.38[a]	1.54	3.18	2.58	Reject
3	3	19.10	43.9[a]	9.05	2.74	2.58	Reject
4	3	20.70	48.5[a]	9.42	2.95	2.58	Reject
3	13	127.00	45.8	24.6	3.30	2.62	Reject
4	13	124.00	50.6	23.3	3.15	2.62	Reject

[a] Rejected after higher value from same ampul was rejected.

STATISTICAL SUMMARIES

After the outlier rejection tests were performed, the following summary statistics were calculated employing the remaining data for each ampul (single analyte, single concentration, single water matrix):

- Number of retained data points, n
- Mean recovery of retained data, $\bar{X}$
- Accuracy as a percent of relative error, % RE
- Overall absolute standard deviation, S
- Percent relative overall standard deviation, % RSD
- Absolute single-analyst standard deviation, SR
- Percent relative single-analyst standard deviation, % RSD-SA

All of these statistics, except the single-analyst absolute and relative standard deviations, were calculated using the retained data for each ampul. The basic statistical formulas used for these calculations are given below, where $X_1, X_2, \ldots, X_n$ denote the values for the n retained data points for a given ampul.

Mean Recovery ($\bar{X}$):

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

Accuracy as a % Relative Error:

$$\% \text{ RE} = \frac{\bar{X} - \text{true value}}{\text{true value}} \times 100 \qquad (6)$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2} \qquad (4)$$

and

Percent Relative Overall Standard Deviation:

$$\% \text{ RSD} = \frac{S}{X} \times 100 \qquad (7)$$

The overall standard deviation, S, indicates the precision associated with measurements generated by a group of laboratories. This represents the broad variation in the data collected in a collaborative study. A measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision, denoted by SR, is measured by

$$SR = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2} \qquad (8)$$

where m = number of retained Youden-paired observations
D_i = difference between observations in the i^{th} pair
$\bar{D}$ = average of D_i values

The Youden-pair design employed in this study permits the calculation of this single-analyst precision without making duplicate measurements on the same sample. This helps to avoid the well-intentioned manipulation of data that can occur when laboratories make duplicate analyses.

The percent relative standard deviation for the single-analyst precision is calculated by

$$\% \text{ RSD-SA} = \frac{SR}{\bar{X}*} \times 100 \qquad (9)$$

where $\bar{X}*$ is the average of the two mean recoveries corresponding to the two ampuls defining the particular Youden pair. These summary statistics are presented in Tables 11 through 17 for each of the seven purgeable aromatic compounds in the six water matrices.

It is often the case that a systematic relationship exists between the mean recovery (X) and the true concentration level (C) of the analyte in the sample. In addition, there are often systematic relationships between the precision statistics (S and SR) and the mean recovery (X). Usually these systematic relationships can be adequately approximated by a linear relationship (i.e., by a straight line). Once these straight lines are established, they can be used to conveniently summarize the behavior of the method within a water type, and they can aid in comparing the behavior of the method across water types. In addition they can be used to obtain estimates of the accuracy and precision at any concentration level within the applicable range studied. They can also be used to predict the behavior of the method when used under similar conditions. These important relationships are discussed below.

Statements of Method Accuracy

The accuracy of the method is characterized by the relationship of the mean recovery (X) to the true concentration (C) of the analyte in the water sample. In order to obtain a mathematical expression

TABLE 11. STATISTICAL SUMMARY FOR BENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	16	17	19	17	16	15	17	18	16	14	15	14
TRUE CONC (C) UG/L	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
MEAN RECOVERY (X)	2.43	3.63	3.11	3.48	2.47	3.06	2.11	2.69	2.33	2.87	2.52	3.37
ACCURACY(%REL ERROR)	10.54	20.90	41.53	15.86	12.30	1.96	-3.96	-10.41	5.71	-4.21	14.70	12.48
OVERALL STD DEV (S)	0.81	1.89	2.08	1.51	0.96	0.85	1.14	1.52	1.37	1.97	1.09	1.61
OVERALL REL STD DEV, %	33.46	52.05	66.74	43.43	38.73	27.67	53.82	56.66	58.89	68.42	43.05	47.79
SINGLE STD DEV, (SR)	0.88		0.30		0.40		0.87		1.14		0.71	
ANALYST REL DEV, %	29.15		8.96		14.65		36.09		43.82		24.09	
MEDIUM YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	16	17	15	17	15	15	19	19	16	18	17	17
TRUE CONC (C) UG/L	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
MEAN RECOVERY (X)	44.01	48.23	46.17	57.09	45.59	50.32	43.86	45.74	42.97	42.90	44.04	48.69
ACCURACY(%REL ERROR)	-4.33	-10.69	0.38	5.72	-0.90	-6.81	-4.66	-15.29	-6.59	-20.56	-4.26	-9.83
OVERALL STD DEV (S)	6.61	8.18	7.77	12.06	6.39	6.03	13.21	13.02	5.88	11.55	11.99	12.55
OVERALL REL STD DEV, %	15.02	16.96	16.82	21.12	14.02	11.99	30.11	28.46	13.69	26.93	27.22	25.78
SINGLE STD DEV, (SR)	3.66		7.04		3.93		5.43		4.73		5.22	
ANALYST REL DEV, %	7.93		13.64		8.20		12.13		11.02		11.26	
HIGH YOUDEN PAIR	5	6	5	6	5	6	5	6	5	6	5	6
NUMBER OF DATA POINTS	18	18	18	18	17	17	19	19	18	18	17	17
TRUE CONC (C) UG/L	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
MEAN RECOVERY (X)	422.83	487.61	433.44	501.83	420.59	493.88	430.79	487.05	400.11	483.67	435.41	509.71
ACCURACY(%REL ERROR)	-6.04	-11.34	-3.68	-8.76	-6.54	-10.20	-4.27	-11.44	-11.09	-12.06	-3.24	-7.33
OVERALL STD DEV (S)	105.23	111.42	120.32	129.49	107.82	136.16	93.00	122.13	117.63	150.60	99.85	119.82
OVERALL REL STD DEV, %	24.89	22.85	27.76	25.80	25.64	27.57	21.59	25.08	29.40	31.14	22.93	23.51
SINGLE STD DEV, (SR)	55.34		38.15		41.68		66.67		44.21		41.83	
ANALYST REL DEV, %	12.16		8.16		9.12		14.53		10.00		8.85	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 12. STATISTICAL SUMMARY FOR CHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	18	17	17	16	17	17	12	9	5	6	17	15
TRUE CONC (C) UG/L	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
MEAN RECOVERY (X)	2.20	2.72	2.30	2.74	1.94	2.48	2.68	6.97	23.40	17.50	2.35	2.52
ACCURACY(%REL ERROR)	0.10	-9.31	4.63	-8.58	-11.84	-17.37	21.63	132.30	963.64	483.33	6.87	-15.84
OVERALL STD DEV (S)	0.48	0.54	0.85	0.64	0.50	0.80	2.76	4.64	21.62	14.92	1.38	1.06
OVERALL REL STD DEV, %	21.81	19.96	36.72	23.28	25.71	32.25	103.00	66.52	92.38	85.28	58.81	42.08
SINGLE STD DEV, (SR)	0.45		0.37		0.32		3.41		17.04		0.68	
ANALYST REL DEV, %	18.34		14.69		14.44		70.77		83.34		28.06	
MEDIUM YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	17	19	16	16	18	18	18	18	18	18	18	18
TRUE CONC (C) UG/L	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
MEAN RECOVERY (X)	44.51	52.54	47.24	53.02	45.43	50.37	42.72	45.54	54.96	45.51	44.62	50.07
ACCURACY(%REL ERROR)	-3.24	-2.70	2.69	-1.82	-1.24	-6.73	-7.14	-15.66	19.48	-15.73	-3.01	-7.27
OVERALL STD DEV (S)	7.47	11.04	9.13	7.67	9.78	10.73	11.92	11.65	36.38	25.97	9.32	10.09
OVERALL REL STD DEV, %	16.77	21.02	19.33	14.47	21.53	21.30	27.91	25.59	66.18	57.08	20.88	20.15
SINGLE STD DEV, (SR)	4.23		6.66		3.72		5.75		16.32		5.69	
ANALYST REL DEV, %	8.71		13.28		7.77		13.04		32.48		12.03	
HIGH YOUDEN PAIR	5	6	5	6	5	6	5	6	5	6	5	6
NUMBER OF DATA POINTS	17	19	16	17	18	19	16	17	17	18	17	18
TRUE CONC (C) UG/L	450.00	551.00	450.00	551.00	450.00	551.00	450.00	551.00	450.00	551.00	450.00	551.00
MEAN RECOVERY (X)	436.29	505.84	411.44	487.53	394.89	485.05	413.38	500.71	400.29	470.83	410.47	492.17
ACCURACY(%REL ERROR)	-3.05	-8.20	-8.57	-11.52	-12.25	-11.97	-8.14	-9.13	-11.05	-14.55	-8.78	-10.68
OVERALL STD DEV (S)	57.27	88.60	65.68	87.49	71.72	80.91	65.13	87.76	108.48	122.01	51.47	72.20
OVERALL REL STD DEV, %	13.13	17.52	15.96	17.95	18.16	16.68	15.76	17.53	27.10	25.91	12.54	14.67
SINGLE STD DEV, (SR)	45.78		31.92		36.52		46.62		68.01		44.67	
ANALYST REL DEV, %	9.72		7.10		8.30		10.20		15.61		9.90	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 13. STATISTICAL SUMMARY FOR 1,2-DICHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	16	14	16	16	12	14	13	16	14	13	13	15
TRUE CONC (C) UG/L	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
MEAN RECOVERY (X)	2.79	2.92	2.59	2.88	2.09	2.99	2.07	3.58	2.78	3.55	1.63	2.11
ACCURACY(%REL ERROR)	26.68	-2.81	17.93	-3.96	-5.04	-0.24	-5.94	19.40	26.56	18.28	-26.12	-29.67
OVERALL STD DEV (S)	1.42	0.84	0.89	0.63	0.33	1.02	0.68	1.95	1.88	1.28	0.71	1.05
OVERALL REL STD DEV, %	50.85	28.98	34.28	21.88	16.03	33.99	32.87	54.42	67.57	35.95	43.40	49.66
SINGLE STD DEV, (SR)	0.45		0.70		0.29		1.23		1.23		0.41	
ANALYST REL DEV, %	15.65		25.57		11.22		43.47		38.72		21.76	
MEDIUM YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	18	18	17	18	17	16	17	17	17	17	16	16
TRUE CONC (C) UG/L	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
MEAN RECOVERY (X)	48.13	49.65	45.41	51.35	45.90	49.18	43.81	48.46	48.44	49.92	42.46	48.22
ACCURACY(%REL ERROR)	4.64	-8.06	-1.28	-4.91	-0.22	-8.92	-4.76	-10.26	5.29	-7.56	-7.70	-10.71
OVERALL STD DEV (S)	11.46	10.64	6.06	7.72	7.37	6.06	7.74	8.43	7.70	10.18	5.12	11.62
OVERALL REL STD DEV, %	23.81	21.43	13.35	15.03	16.05	12.31	17.67	17.40	15.89	20.40	12.05	24.09
SINGLE STD DEV, (SR)	9.10		4.24		4.10		5.12		5.82		7.96	
ANALYST REL DEV, %	18.62		8.77		8.63		11.09		11.83		17.55	
HIGH YOUDEN PAIR	5	6	5	6	5	6	5	6	5	6	5	6
NUMBER OF DATA POINTS	18	18	18	18	17	16	18	18	17	17	16	16
TRUE CONC (C) UG/L	449.00	600.00	449.00	600.00	449.00	600.00	449.00	600.00	449.00	600.00	449.00	600.00
MEAN RECOVERY (X)	447.17	500.17	427.06	488.11	394.24	466.38	409.28	477.50	444.94	528.71	420.69	467.13
ACCURACY(%REL ERROR)	-0.41	-16.64	-4.89	-18.65	-12.20	-22.27	-8.85	-20.42	-0.90	-11.88	-6.31	-22.15
OVERALL STD DEV (S)	80.27	128.63	91.39	111.21	89.13	88.35	124.17	132.22	94.58	99.06	80.50	80.80
OVERALL REL STD DEV, %	17.95	25.72	21.40	22.78	22.61	18.94	30.34	27.69	21.26	18.74	19.14	17.30
SINGLE STD DEV, (SR)	74.18		55.06		47.15		54.35		51.16		53.13	
ANALYST REL DEV, %	15.66		12.03		10.96		12.26		10.51		11.97	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 14. STATISTICAL SUMMARY FOR 1,3-DICHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	15	16	15	15	18	17	7	9	13	11	15	15
TRUE CONC (C) UG/L	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
MEAN RECOVERY (X)	2.07	2.78	2.36	2.82	2.60	2.89	3.40	10.39	2.85	2.62	2.18	3.02
ACCURACY(%REL ERROR)	-5.73	-7.23	7.12	-6.13	18.11	-3.57	54.55	246.44	29.55	-12.82	-1.00	0.71
OVERALL STD DEV (S)	0.46	0.67	0.84	0.53	1.47	1.07	1.80	7.05	1.42	1.20	0.79	0.89
OVERALL REL STD DEV, %	22.20	23.93	35.49	18.94	56.73	36.91	52.90	67.80	49.75	45.74	36.50	29.43
SINGLE STD DEV, (SR)	0.26		0.54		0.30		1.44		0.79		0.59	
ANALYST REL DEV, %	10.86		20.95		10.94		20.91		28.82		22.79	
MEDIUM YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	19	19	17	17	18	18	17	18	18	17	17	17
TRUE CONC (C) UG/L	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
MEAN RECOVERY (X)	47.65	51.74	45.98	54.52	46.15	52.44	42.85	53.88	43.86	49.14	43.94	52.81
ACCURACY(%REL ERROR)	3.58	-4.19	-0.05	0.97	0.33	-2.88	-6.85	-0.23	-4.65	-9.01	-4.49	-2.20
OVERALL STD DEV (S)	11.13	9.68	6.34	7.36	7.12	8.71	16.51	22.16	6.31	9.49	5.45	9.62
OVERALL REL STD DEV, %	23.36	18.71	13.79	13.51	15.43	16.61	38.52	41.12	14.40	19.31	12.39	18.21
SINGLE STD DEV, (SR)	9.13		4.30		4.85		9.31		3.53		6.23	
ANALYST REL DEV, %	18.37		8.55		9.83		19.24		7.59		12.88	
HIGH YOUDEN PAIR	5	6	5	6	5	6	5	6	5	6	5	6
NUMBER OF DATA POINTS	18	18	16	17	18	18	18	17	18	18	17	17
TRUE CONC (C) UG/L	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
MEAN RECOVERY (X)	443.89	473.06	399.50	478.94	412.44	487.11	413.85	501.82	433.78	502.50	421.82	482.06
ACCURACY(%REL ERROR)	-1.36	-13.99	-11.22	-12.92	-8.35	-11.43	-8.03	-8.76	-3.60	-8.64	-6.26	-12.35
OVERALL STD DEV (S)	68.58	87.59	61.56	94.42	99.85	97.72	126.26	115.09	98.84	105.15	82.61	77.83
OVERALL REL STD DEV, %	15.45	18.52	15.41	19.71	24.21	20.06	30.51	22.93	22.79	20.93	19.58	16.15
SINGLE STD DEV, (SR)	54.70		36.47		49.18		52.98		60.60		50.93	
ANALYST REL DEV, %	11.93		8.30		10.93		11.57		12.94		11.27	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 15. STATISTICAL SUMMARY FOR 1,4-DICHLOROBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	16	16	15	16	18	18	10	11	11	15	14	16
TRUE CONC (C) UG/L	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
MEAN RECOVERY (X)	2.04	2.57	2.32	2.84	2.22	2.84	2.42	3.35	2.01	3.95	2.06	2.93
ACCURACY(%REL ERROR)	-7.41	-14.48	5.58	-5.40	0.86	-5.48	9.86	11.67	-8.51	31.62	-6.53	-2.42
OVERALL STD DEV (S)	0.90	0.82	0.87	0.60	1.28	1.24	1.01	1.22	0.70	1.93	0.46	1.13
OVERALL REL STD DEV, %	44.21	31.83	37.46	21.12	57.82	43.57	41.99	36.39	34.64	48.91	22.39	38.57
SINGLE STD DEV, (SR)	0.63		0.62		0.24		1.07		1.15		0.57	
ANALYST REL DEV, %	27.28		23.95		9.36		37.21		38.52		22.72	
MEDIUM YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	19	19	16	17	18	18	17	18	17	18	17	17
TRUE CONC (C) UG/L	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
MEAN RECOVERY (X)	46.96	50.30	44.16	52.59	44.77	48.69	42.51	48.11	45.85	51.01	42.10	51.42
ACCURACY(%REL ERROR)	2.09	-6.85	-4.01	-2.60	-2.68	-9.84	-7.58	-10.92	-0.33	-5.53	-8.48	-4.77
OVERALL STD DEV (S)	12.63	9.07	4.74	6.91	6.18	6.95	7.22	8.57	5.31	9.28	4.48	7.12
OVERALL REL STD DEV, %	26.89	18.02	10.73	13.13	13.81	14.28	16.99	17.81	11.57	18.19	10.63	13.85
SINGLE STD DEV, (SR)	8.76		4.63		5.59		2.78		5.37		4.47	
ANALYST REL DEV, %	18.00		9.57		11.96		6.14		11.09		9.56	
HIGH YOUDEN PAIR	5	6	5	6	5	6	5	6	5	6	5	6
NUMBER OF DATA POINTS	19	19	17	17	18	18	18	17	18	18	17	17
TRUE CONC (C) UG/L	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
MEAN RECOVERY (X)	421.68	474.63	395.82	464.88	377.17	446.33	394.83	478.00	417.00	491.89	403.35	476.88
ACCURACY(%REL ERROR)	-6.29	-13.70	-12.04	-15.48	-16.19	-18.85	-12.26	-13.09	-7.33	-10.57	-10.37	-13.29
OVERALL STD DEV (S)	67.58	112.18	70.12	91.16	81.51	94.45	85.81	88.21	87.57	87.78	75.96	66.87
OVERALL REL STD DEV, %	16.03	23.63	17.71	19.61	21.61	21.16	21.73	18.45	21.00	17.84	18.83	14.02
SINGLE STD DEV, (SR)	60.22		39.38		45.86		46.05		50.12		42.54	
ANALYST REL DEV, %	13.44		9.15		11.14		10.55		11.03		9.67	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 16. STATISTICAL SUMMARY FOR ETHYLBENZENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	18	16	16	16	15	15	17	16	15	17	14	14
TRUE CONC (C) UG/L	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
MEAN RECOVERY (X)	2.46	2.93	2.66	3.07	2.21	3.03	2.49	3.07	2.18	2.46	3.15	2.54
ACCURACY(%REL ERROR)	11.87	-2.35	20.82	2.42	0.30	1.09	13.40	2.46	-1.12	-17.86	43.31	-15.45
OVERALL STD DEV (S)	0.96	0.88	1.27	1.25	0.81	1.05	0.97	1.00	0.82	1.46	1.37	1.31
OVERALL REL STD DEV, %	38.89	29.90	47.65	40.66	36.64	34.54	38.74	32.68	37.82	59.12	43.36	51.47
SINGLE STD DEV, (SR)	0.91		0.48		0.53		0.73		0.70		0.89	
ANALYST REL DEV, %	33.68		16.79		20.38		26.06		30.15		31.38	
MEDIUM YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	18	18	16	18	17	17	17	17	17	18	18	18
TRUE CONC (C) UG/L	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
MEAN RECOVERY (X)	46.43	53.39	47.19	58.20	46.35	51.20	45.16	53.99	43.05	46.13	43.77	49.80
ACCURACY(%REL ERROR)	0.93	-1.12	2.58	7.78	0.75	-5.19	-1.83	-0.02	-6.41	-14.58	-4.86	-7.78
OVERALL STD DEV (S)	15.80	16.07	9.14	13.69	9.69	10.49	9.95	13.67	8.39	16.12	11.50	11.15
OVERALL REL STD DEV, %	34.04	30.09	19.36	23.52	20.91	20.49	22.04	25.32	19.49	34.96	26.27	22.39
SINGLE STD DEV, (SR)	13.05		5.74		4.00		6.82		5.36		8.08	
ANALYST REL DEV, %	26.14		10.90		8.20		13.75		12.02		17.27	
HIGH YOUDEN PAIR	5	6	5	6	5	6	5	6	5	6	5	6
NUMBER OF DATA POINTS	18	17	18	18	17	17	17	17	18	18	18	18
TRUE CONC (C) UG/L	452.00	551.00	452.00	551.00	452.00	551.00	452.00	551.00	452.00	551.00	452.00	551.00
MEAN RECOVERY (X)	421.39	470.82	419.94	488.33	397.53	484.18	405.88	492.06	390.28	459.83	412.83	493.67
ACCURACY(%REL ERROR)	-6.77	-14.55	-7.09	-11.37	-12.05	-12.13	-10.20	-10.70	-13.66	-16.55	-8.67	-10.41
OVERALL STD DEV (S)	91.24	101.12	89.50	100.85	90.10	107.74	80.03	104.13	88.23	106.06	74.93	87.28
OVERALL REL STD DEV, %	21.65	21.48	21.31	20.65	22.67	22.25	19.72	21.16	22.61	23.06	18.15	17.68
SINGLE STD DEV, (SR)	42.69		46.57		34.50		53.57		45.46		46.84	
ANALYST REL DEV, %	9.57		10.25		7.83		11.93		10.70		10.33	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

TABLE 17. STATISTICAL SUMMARY FOR TOLUENE ANALYSES BY WATER TYPE

	WATER 1		WATER 2		WATER 3		WATER 4		WATER 5		WATER 6	
LOW YOUDEN PAIR	1	2	1	2	1	2	1	2	1	2	1	2
NUMBER OF DATA POINTS	19	16	16	17	16	18	14	17	6	9	15	13
TRUE CONC (C) UG/L	2.10	3.00	2.10	3.00	2.10	3.00	2.10	3.00	2.10	3.00	2.10	3.00
MEAN RECOVERY (X)	2.81	3.08	2.14	2.96	1.91	2.93	2.86	3.48	12.47	5.96	2.99	3.56
ACCURACY(%REL ERROR)	33.81	2.62	2.14	-1.47	-9.20	-2.17	36.12	15.94	494.05	98.59	42.60	18.74
OVERALL STD DEV (S)	1.65	0.70	0.66	0.67	0.50	1.76	1.12	1.90	11.28	5.40	1.77	2.87
OVERALL REL STD DEV, %	58.84	22.87	30.94	22.75	26.27	60.02	39.29	54.71	90.39	90.61	59.09	80.66
SINGLE STD DEV, (SR)	0.75		0.43		0.38		1.40		5.03		1.53	
ANALYST REL DEV, %	25.57		16.97		15.90		44.33		54.53		46.52	
MEDIUM YOUDEN PAIR	3	4	3	4	3	4	3	4	3	4	3	4
NUMBER OF DATA POINTS	16	17	16	17	18	18	19	19	17	14	18	18
TRUE CONC (C) UG/L	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
MEAN RECOVERY (X)	44.31	50.72	44.82	53.24	43.76	49.49	41.12	46.44	52.53	42.72	42.66	48.52
ACCURACY(%REL ERROR)	-3.67	-6.08	-2.55	-1.41	-4.87	-8.34	-10.62	-14.01	14.19	-20.89	-7.26	-10.15
OVERALL STD DEV (S)	6.64	9.62	8.73	10.19	10.17	11.44	7.86	11.82	22.87	7.01	11.13	10.73
OVERALL REL STD DEV, %	15.00	18.96	19.47	19.14	23.25	23.12	19.13	25.45	43.54	16.40	26.09	22.13
SINGLE STD DEV, (SR)	4.15		6.16		3.61		5.79		15.16		6.38	
ANALYST REL DEV, %	8.73		12.56		7.75		13.23		31.82		14.00	
HIGH YOUDEN PAIR	5	6	5	6	5	6	5	6	5	6	5	6
NUMBER OF DATA POINTS	17	18	17	17	18	18	19	19	17	17	18	18
TRUE CONC (C) UG/L	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
MEAN RECOVERY (X)	444.59	515.00	417.29	483.29	418.06	495.78	407.63	470.89	398.82	499.65	425.22	500.89
ACCURACY(%REL ERROR)	-1.20	-6.36	-7.27	-12.13	-7.10	-9.86	-9.42	-14.38	-11.37	-9.16	-5.51	-8.93
OVERALL STD DEV (S)	81.63	114.73	102.40	107.78	99.38	106.17	109.98	127.12	106.88	149.77	85.97	100.63
OVERALL REL STD DEV, %	18.36	22.28	24.54	22.30	23.77	21.42	26.98	27.00	26.80	29.98	20.22	20.09
SINGLE STD DEV, (SR)	52.11		36.57		42.12		51.12		60.17		41.19	
ANALYST REL DEV, %	10.86		8.12		9.22		11.64		13.39		8.90	

WATER LEGEND

1 - DISTILLED WATER
2 - TAP WATER
3 - SURFACE WATER
4 - WASTE WATER 1
5 - WASTE WATER 2
6 - WASTE WATER 3

for this relationship, a regression line of the form

$$\bar{X} = a + b \cdot C \qquad (10)$$

was fitted to the data by regression techniques.

It is often the case that the true concentration values vary over a wide range. In such cases, the mean recovery statistics associated with the larger concentration values tend to dominate the fitted regression line producing relatively larger errors in the estimates of mean recovery at the lower concentration values. In order to eliminate this problem, a weighted least squares technique was used to fit the mean recovery data to the true concentration values. The weighted least squares technique was performed by dividing both sides of Equation (10) by C resulting in Equation (11).

$$\frac{\bar{X}}{C} \quad a \cdot \frac{1}{C} + b \qquad (11)$$

If the intercept "b" associated with the fitted line is negligible (i.e., essentially zero), then the slope "a" provides a unique value which represents the percent recovery over all of the concentration levels.

Statements of Method Precision

The precision of the method is characterized by the relationships between precision statistics (S and SR) and mean recovery ($\bar{X}$). In order to obtain a mathematical expression for these relationships, regression lines of the form

$$S = d + e \cdot \bar{X} \tag{12}$$

and

$$SR = f + g \cdot X^* \tag{13}$$

were fitted to the data.

As discussed previously with respect to accuracy, the values of $\bar{X}$ and X^* often vary over a wide range. In such cases the standard deviation statistics associated with the larger mean recovery values will dominate the regression lines. This will produce relatively larger errors in the estimates of S and SR at the lower mean recovery values. Therefore, a weighted least squares technique was also used to establish the values of the parameters d, e, f, and g in Equations (12) and (13). The weighted least squares technique was performed by dividing both sides of Equation (12) by X resulting in Equation (14)

$$\frac{S}{X} = d \cdot \frac{1}{X} + e \tag{14}$$

and by dividing both sides of Equation (13) by X^* resulting in Equation (15)

$$\frac{SR}{X^*} = f \cdot \frac{1}{X^*} + g \quad . \tag{15}$$

If the intercepts, e and g, are negligible, then the slopes, d and f, are good approximations to the overall and single-analyst percent relative standard deviations, respectively. These, in turn, are measures of the method precision.

COMPARISON OF ACCURACY AND PRECISION ACROSS WATER TYPES

It is possible that the accuracy and precision of Method 602 depend on the water type analyzed. The summary statistics $\bar{X}$, S, and SR are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on accuracy and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome because there are 36 mean recovery statistics ($\bar{X}$) (six ampuls x six waters), 36 overall precision statistics (S), and 18 single-analyst precision statistics (SR) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldy. Second, the statistical properties of this type of comparison procedure are difficult to determine. Finally, due to variation associated with $\bar{X}$, S, and SR, comparisons based on these statistics can lead to inconsistent conclusions about the effect of water type. For example, distilled water may appear to produce a significantly lower value than drinking water for the precision statistic S at a high concentration, but a significantly higher value for S at a low concentration.

An alternative approach [2], has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is calculated using the following statistical model. If X_{ijk} denotes the measurement reported by laboratory "i," for water type "j," and ampul "k," then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk} \qquad (1)$$

where $i = 1,2,\ldots, n$
$j = 1,2$
$k = 1,2,\ldots, 6$

Model components β_j and γ_j are fixed parameters that determine the effect of water type j on the behavior of the observed measurements (X_{ijk}). The parameter C_k is the true concentration level associated with ampul "k." The model component L_i is a random factor which accounts for the systematic error associated with laboratory "i." The model component ε_{ijk} is the random factor that accounts for the intralaboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data (X_{ijk}) and the true concentration level (C_k) through the use of the exponent γ_j on C_k. This makes the model more flexible in comparison to straight-line models. Second, as will be noted below, an inherent increasing relationship exists between the variability in the data and the concentration level C_k in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Accuracy is related directly to the mean recovery or expected value of the measurements (X_{ijk}). The expected value for the data modeled by Equation 1 is

$$E(X_{ijk}) = \beta_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \varepsilon_{ijk}) \qquad (16)$$

Precision is related to the variability in the measurements (X_{ijk}). The variance of the data modeled by Equation 1 is

$$\mathrm{Var}(X_{ijk}) = \left[\beta_j \cdot C_k^{\gamma_j}\right]^2 \mathrm{Var}(L_i \cdot \varepsilon_{ijk}), \qquad (17)$$

which is an increasing function of C_k. (See Reference 2 for a complete discussion of this model.)

The accuracy and precision of Method 602 depend upon water type through Equations 16 and 17 and the parameters β_j and γ_j. If β_j and γ_j vary with j (i.e., vary across water type), then the accuracy and precision of the method also vary across water type.

To determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation 1 represents the basic model. However, taking natural logarithms of both sides of Equation 1, the following straight line regression model is obtained.

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \qquad (2)$$

The parameter $\ell n\, \beta_j$ is the intercept, and γ_j is the slope of the regression line associated with water type "j." It is assumed that $\ell n\, L_i$ is normally distributed with mean 0 and variance σ_L^2, that $\ell n\, \varepsilon_{ijk}$ is normally distributed with mean 0 and variance σ_ε^2, and that the $\ell n\, L_i$ and $\ell n\, \varepsilon_{ijk}$ terms are independent.

Based on Equation 2, the comparison of water types reduces to the comparison of straight lines. Distilled water is viewed as a control, and each of the remaining lines is compared directly to the line for distilled water.

Using the data on the log-log scale and regression techniques, the parameter $\ell n\ \beta_j$ (and hence β_j) and γ_j can be estimated. These estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative hypothesis, H_O and H_A, respectively are given by:

$$H_O:\ \ell n\ \beta_j - \ell n\ \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2 \tag{18}$$

$$H_A:\ \ell n\ \beta_j - \ell n\ \beta_1 \neq 0 \text{ and/or } \gamma_j - \gamma_1 \neq 0 \text{ for some } j = 2 \tag{19}$$

The null hypothesis (H_O) is tested against the alternative hypothesis (H_A) using an F-statistic. The probability of obtaining the value of an F-statistic as large as the value which was actually observed, Prob(F > F OBS), is calculated under the assumption that H_O is true. H_O is rejected in favor of H_A if Prob(F > F OBS) is less than 0.05.

If H_O is not rejected, then there is no evidence in the data that the β_j vary with "j" or that the γ_j vary with "j." Therefore, there is no evidence of an effect due to water type on the accuracy or precision of the method. If H_O is rejected, then some linear combination of the differences ($\ell n\ \beta_j - \ell n\ \beta$) and ($\gamma_j - \gamma_1$) is statistically different from zero. However this does not guarantee there will be a statistically significant direct effect attributable to any specific water type since the overall F test can be overly sensitive to minor systematic effects common to several water types. The effect due to water type is judged to be statistically significant only if one of the differences, ($\ell n\ \beta_j - \ell n\ \beta_1$) and/or ($\gamma_j - \gamma_1$), is statistically different from zero. This is determined by checking the simultaneous 95% confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95% confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is significantly different from zero.

If at least one of the confidence intervals for the differences ($\ln \beta_j - \ln \beta_1$) or ($\gamma_j - \gamma_1$) fails to include zero, then the statistical significance of the effect due to water type has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the differences.

The interpretation of the differences involves comparing the mean recovery and standard deviation for each water type to the mean recovery and standard deviation obtained for distilled water. These comparisons are made on a relative basis. The mean recovery for water type "j," given by Equation 16, is compared to that for distilled water (j = 1) on a relative basis by

$$\frac{E(X_{ijk})}{E(X_{i1k})} = \frac{\beta_j \, C_k^{\gamma_j} \, E(L_i \cdot \varepsilon_{ijk})}{\beta_1 \, C_k^{\gamma_1} \, E(L_i \cdot \varepsilon_{i1k})} = \frac{\beta_j}{\beta_1} C_k^{(\gamma_j - \gamma_1)} \qquad (20)$$

(The ratio of the standard deviations would be equivalent to Equation 20; therefore, the interpretation of the effect on precision is the same as that for the effect on mean recovery.)

The ratio in Equation 20 is a measure of the relative difference in mean recovery between water type "j" and distilled water. It is composed of two parts (a) β_j/β_1, which is independent of the true concentration level (i.e., the constant bias), and (b) $C_k^{(\gamma_j - \gamma_1)}$, which depends on the true concentration level (i.e., the concentration dependent bias). If ($\gamma_j - \gamma_1$) is zero, then the relative difference in mean recovery is β_j/β_1, which is independent of concentration level C_k. Then the mean recovery of water type "j" is β_j/β_1 x 100 percent of the mean recovery for distilled water. If

$(\gamma_j - \gamma_1)$ is not zero, then the mean recovery of water type "j" is $([\beta_j/\beta_1]\cdot C_k^{[\gamma_j - \gamma_1]})$ x 100% of that for distilled water, and therefore depends on the true concentration level C_k.

To illustrate these points, consider the following example. Suppose that a significant F-value has been obtained, and the confidence intervals for all of the differences contain zero except for water type 5. For water type 5, the point estimate for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ is -0.38, and the confidence interval for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ is (-0.69, -0.07). The point estimate for $(\gamma_5 - \gamma_1)$ is -0.07, and the confidence interval for $(\gamma_5 - \gamma_1)$ is (-0.04, 0.18). In this case, a statistically significant effect due to water type has been established that involves only water type 5. The practical significance of this effect is judged by considering Equation 20. The ratio of mean recoveries for water type 5 and distilled water is given by

$$\frac{E(X_{i5k})}{E(K_{i1k})} = \frac{\beta_5}{\beta_1} C_k^{(\gamma_5 - \gamma_1)} \qquad (21)$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{Var(X_{ijk})}{Var(X_{i1k})}} = \frac{\beta_5}{\beta_1} C_k^{(\gamma_5 - \gamma_1)} \qquad (22)$$

Because the confidence interval for $(\gamma_5 - \gamma_1)$ contains zero, this difference is assumed to be insignificant and is set to zero. Therefore, Equations 21 and 22 reduce to β_5/β_1. The point estimate for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ was -0.38. Therefore, the point estimate for β_5/β_1 is 0.68, and the mean recovery for water type 5 is estimated to be 68% of the mean recovery for distilled water. Similarly, the standard deviation for the data for water type 5 is estimated to be 68% of the standard deviation for distilled water. Since the 95% confidence interval for $(\ell n\ \beta_5 - \ell n\ \beta_1)$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for β_5/β_1, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50% to 93% of the mean recovery (standard deviation) for distilled water. The practical significance of the effect due to water type 5 would depend on the importance of a mean recovery (standard deviation) that is between 50% and 93% of the mean recovery (standard deviation) observed for distilled water.

The comparison of accuracy and precision across water types just discussed, is based on the assumption that Equation (1) approximately models the data. It is clear that in practical monitoring programs of this type such models cannot model the data completely in every case. This analysis, therefore, is viewed as a screening procedure which identifies those cases where differences in water types are likely to be present. A more detailed, local analysis can then be pursued using the basic summary statistics for precision and accuracy.

Results of the accuracy and precision comparison among the waters in the study are presented in Appendix G.

SECTION 6

RESULTS AND DISCUSSION

The objective of this study was to characterize the performance of Method 602 in terms of accuracy, overall precision, single-analyst precision, and the effect of water type on accuracy and precision.

One measure of the performance of the method is that 17% of the 5040 analytical values were rejected as outliers, which is equivalent to rejecting data from about three of the twenty laboratories. The 17% level of data rejection is normal for this type of study and is acceptable. Of the 17% outliers, 10% were rejected through application of Youden's laboratory ranking procedure and 7% were rejected employing the Thompson T-test.

ACCURACY

The accuracy of Method 602 is obtained by comparing the mean recovery, $\bar{x}$, to the true values of concentration in µg/L. In Tables 11 through 17, individual values of accuracy as percent relative error are listed for each analyte, in each water matrix, and at each of the six concentration levels in that water matrix (three Youden pairs). This results in 252 separate values for accuracy. The linear regression of mean recovery, $\bar{x}$, versus true concentration level, c, provides values representing the percent recovery over all of the concentration levels. This reduces the separate values for accuracy to 42, one value for each of seven analytes in each of six waters. Table 18 presents the percent recovery for each compound in water types as measured by the slopes of the linear equations for recovery presented earlier in Table 1.

TABLE 18. METHOD 602 ACCURACY

Compound	Water 1		Water 2		Water 3	
	Regression slope[a]	Average recovery[b]	Regression slope	Average recovery	Regression slope	Average recovery
Benzene	92	100	97	109	93	98
Chlorobenzene	95	97	94	96	92	90
1,2-Dichlorobenzene	93	96	91	96	89	92
1,3-Dichlorobenzene	96	95	93	96	93	99
1,4-Dichlorobenzene	93	93	91	94	88	91
Ethylbenzene	94	98	97	103	93	95
Toluene	94	103	94	97	93	93
Average analyte	94	97	94	99	92	94

(continued)

TABLE 18 (continued)

Compound	Water 4		Water 5		Water 6		Average all waters	
	Regression[a] slope	Average[b] recovery	Regression slope	Average recovery	Regression slope	Average recovery	Regression slope	Average recovery
Benzene	91	91	87	92	93	100	92	98
Chlorobenzene	93[c]	119[c]	63[c]	337[c]	92	94	88	138
1,2-Dichlorobenzene	90	95	95	105	88	83	91	95
1,3-Dichlorobenzene	100[c]	146[c]	92	99	94	96	95	105
1,4-Dichlorobenzene	89	96	95	100	91	92	91	94
Ethylbenzene	94	99	86	88	89	99	92	97
Toluene	87	101	71[c]	194[c]	91	105	88	116
Average analyte	92	107	84	145	91	96		

[a] Slope of regression equation for $\overline{X}$ in Table 36.

[b] Average of mean recoveries calculated from Tables 29 through 35.

[c] Differences in accuracy values >±15%.

This is a simplified approach because the intercept portion of the regression equation is assumed to be insignificant. The values are compared to percent recoveries calculated from the average of the quotients $\bar{x}$:c presented in Tables 11 through 17.

Table 18 shows that the percent recoveries (accuracies) calculated by the two methods are in substantial agreement. Minor discrepancies of approximately 10% can be traced to the lowest Youden-pair concentrations. These slightly higher percent recoveries are due to small amounts of interferences added to small amounts of spiked compound. This shows the need and value of the weighted regression equation concept. Simple averaging places too much emphasis on the lowest Youden pair. Major discrepancies do occur in water 5 for chlorobenzene and toluene. These discrepancies can be traced to the extremely high average recoveries of these analytes in the low Youden-pair ampuls for water 5 as presented in Tables 12 and 17 (percent recoveries of 1064 and 583 for chlorobenzene, and 594 and 199 for toluene at the low concentrations). This is attributed to high background or blank values of chlorobenzene and toluene in water 5 (average of 226 µg/L for chlorobenzene and 127 µg/L for toluene over the 20 laboratories). The mean recovery for chlorobenzene and toluene for the middle and high Youden-pair concentration are 94.5% and 86.4%, respectively.

Large discrepencies are also noted for chlorobenzene and 1,3-dichlorobenzene in water 4 where the average blank values of these analytes were 28.9 µg/L and 42.8 µg/L, respectively. While these background concentrations are lower than those for chlorobenzene and toluene in water 5 they are sufficiently high to cause unnaturally high recoveries in the low Youden pair concentrations (see Tables 12 and 14). In addition the intercepts of the linear regression equations for chlorobenzene and 1,3-dichlorobenzene in water 4 and chlorobenzene and toluene in water 5 cannot be considered negligible since they represent a significant percentage of the average values for accuracy as calculated from the data in Tables 12, 14, and 17 (this is presented later in Table 23). Of all possible combinations of analyte and water these four cases are the only ones where the intercept value exceeds one percent of the average value of accuracy.

PRECISION

The overall and single-analyst precisions of Method 602 were determined as percent relative standard deviations for each analyte, water type, and concentration level. As presented in Tables 11 through 17, 252 individual values of overall percent relative standard deviation and 126 individual values of single-analyst percent relative standard deviation result. The linear regression of standard deviation, s, versus mean recovery, $\bar{x}$, provides values of percent relative standard deviation over all the concentration ranges. This reduces the separate measures of precision to 42, one value for each of seven analytes in each of six water-types. Tables 19 and 20 present the percent relative standard deviations as measured by the slopes of the linear regression equations presented earlier in Table 1 for the overall and the single-analyst precision, respectively. These values are compared to the averages of the percent relative standard deviatons presented in Tables 11 through 17.

In general, the linear regression slope yields higher precision values (lower percent relative standard deviation). The major discrepencies in the precision values (% RSD and % RSD-SA) occur for chlorobenzene in waters 4 and 5 and for toluene in waters 5 and 6. These differences can be traced to the low precision of measurements for toluene and chlorobenzene in the low Youden-pair analyses (see Tables 12 and 17). These poor precision values also can be attributed to the high background concentrations for chlorobenzene in water 5 and toluene in waters 5 and 6 (see Appendix E) and subsequent variability in the values corrected for background (blank value).

TABLE 19. METHOD 602 PRECISION (% RSD)

Compound	Water 1		Water 2		Water 3	
	Regression[a] slope	Average[b] % RSD	Regression slope	Average % RSD	Regression slope	Average % RSD
Benzene	21	28	22	34	19	24
Chlorobenzene	17	18	16	21	19	23
1,2-Dichlorobenzene	22	28	18	21	18	20
1,3-Dichlorobenzene	19	20	15	19	18	28
1,4-Dichlorobenzene	20	27	15	20	17	29
Ethylbenzene	26	29	20	29	21	26
Toluene	18	26	21	23	25	30
Average analyte	20	25	18	24	20	26

(continued)

TABLE 19 (continued)

Compound	Water 4		Water 5		Water 6		Average all waters	
	Regression[a] slope	Average[b] % RSD	Regression slope	Average % RSD	Regression slope	Average % RSD	Regression slope	Average % RSD
Benzene	26	36	25	38	25	32	23	32
Chlorobenzene	21[c]	43[c]	31[c]	59[c]	16	28	20	32
1,2-Dichlorobenzene	25	30	17	30	18	28	20	26
1,3-Dichlorobenzene	36	42	19	29	16	22	21	27
1,4-Dichlorobenzene	18	26	19	25	15	20	17	25
Ethylbenzene	21	27	25	33	20	30	22	29
Toluene	24	32	28[c]	50[c]	21[c]	38[c]	23	33
Average analyte	24	34	23	38	19	28		

[a] Slope of regression equation for S in Table 36.

[b] Average of % RSD values in Tables 29 through 35.

[c] Differences in prevision values exceed 15 units.

TABLE 20. METHOD 602 PRECISION (% RSD-SA)

Compound	Water 1		Water 2		Water 3	
	Regression slope[a]	Average % RSD-SA[b]	Regression slope	Average % RSD-SA	Regression slope	Average % RSD-SA
Benzene	9	16	11	11	8	11
Chlorobenzene	9	12	10	12	8	10
1,2-Dichlorobenzene	17	17	10	15	10	11
1,3-Dichlorobenzene	15	14	8	13	10	11
1,4-Dichlorobenzene	15	20	9	14	12	11
Ethylbenzene	17	23	10	13	8	12
Toluene	9	15	10	13	8	11
Average analyte	13	17	10	13	9	11

(continued)

TABLE 20 (continued)

Compound	Water 4		Water 5		Water 6		Average all waters	
	Regression[a] slope	Average[b] % RSD-SA	Regression slope	Average % RSD-SA	Regression slope	Average % RSD-SA	Regression slope	Average % RSD-SA
Benzene	13	21	9	23	10	15	10	16
Chlorobenzene	8[c]	31[c]	9[c]	44[c]	10	17	9	21
1,2-Dichlorobenzene	11	22	10	20	15	17	12	17
1,3-Dichlorobenzene	15	17	10	16	12	16	12	15
1,4-Dichlorobenzene	7	18	10	20	9	14	10	16
Ethylbenzene	12	17	11	18	13	20	12	17
Toluene	11	23	18[c]	33[c]	10[c]	23[c]	11	20
Average analyte	11	21	13	25	11	17		

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[a] Slope of regression equation for S_r in Table 36.

[b] Average of %RSD-SA values in Tables 29 through 35.

[c] Differences in precision values exceed 15 units.

These same analyte/water combinations exhibit the largest intercepts in the linear regression equations for S and SR as shown later in Table 23. In each of these cases the intercepts exceed 5% of the average values of S and SR calculated from the data in Tables 11 through 17.

The preceding regression equations presented in Table 1 assume a linear relationship between the precision of the data and the concentration of the analytes. A summary of % RSD and % RSD-SA in each of the Youden-pair concentrations is presented in Tables 21 and 22, in order to examine the assumption of a linear relationship. It is apparent from these tables that the average precision is low for the low Youden-pair samples (high values of % RSD and % RSD-SA), but that the precision values for the medium and high Youden-pair concentrations are comparable. The low precision values at low concentrations are especially evident in the cases of the wastewater matrices (waters 4 through 6). In these cases a curvalinier relationship for % RSD and % RSD-SA appears to exist.

As a test of the relative magnitudes of the intercept values, average values of S, SR, and $\bar{X}$ were calculated from the data in Tables 11 through 17 over the three concentration levels reported in this study. Table 23 presents the average values for the statistical quantities and the percentage of these averages represented by the intercepts from the linear regression equations presented in Table 1. From the data presented in Table 23, it is apparent that non-negligible values of the intercepts occur for chlorobenzene in wastewaters 1 and 2 (waters 4 and 5), and for toluene in wastewater 2 (water 5). These cases and other scattered cases in the table bring to question whether the slopes of the linear regression equations represent good approximations of the accuracy and/or precision of Method 602 over the concentration range investigated.

TABLE 21. SUMMARY OF PRECISION (% RSD) BY ANALYTE, WATER TYPE, AND CONCENTRATION LEVEL

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Distilled water	Benzene	42.7	16.0	23.9
	Chlorobenzene	20.9	18.9	15.3
	1,2-Dichlorobenzene	39.9	22.6	21.8
	1,3-Dichlorobenzene	23.1	21.0	17.4
	1,4-Dichloorbenzene	38.0	22.5	19.8
	Ethylbenzene	34.4	32.1	21.6
	Toluene	40.9	17.0	20.3
	Average of all analytes	34.3	21.4	20.0
Tap water	Benzene	55.0	9.9	26.8
	Chlorobenzene	30.0	16.9	17.0
	1,2-Dichlorobenzene	28.1	14.2	22.1
	1,3-Dichlorobenzene	27.2	13.7	17.6
	1,4-Dichloorbenzene	29.3	11.9	18.7
	Ethylbenzene	44.2	21.4	21.0
	Toluene	26.9	19.3	23.4
	Average of all analytes	34.4	15.3	20.9
Surface water	Benzene	33.2	13.0	26.6
	Chlorobenzene	29.0	21.4	17.4
	1,2-Dichlorobenzene	25.0	14.2	20.8
	1,3-Dichlorobenzene	46.8	16.0	22.1
	1,4-Dichloorbenzene	50.7	14.1	21.4
	Ethylbenzene	35.6	20.7	22.5
	Toluene	43.2	23.2	22.6
	Average of all analytes	37.6	17.5	21.9

(continued)

TABLE 21 (continued)

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Wastewater 1	Benzene	55.2	29.3	23.3
	Chlorobenzene	84.8	26.8	16.7
	1,2-Dichlorobenzene	43.7	17.5	29.0
	1,3-Dichlorobenzene	60.4	39.8	26.7
	1,4-Dichloorbenzene	39.2	17.4	20.1
	Ethylbenzene	35.7	23.7	20.4
	Toluene	47.0	22.3	27.0
	Average of all analytes	52.3	25.3	23.3
Wastewater 2	Benzene	63.7	20.3	30.3
	Chlorobenzene	88.8	61.6	26.5
	1,2-Dichlorobenzene	51.8	18.2	20.0
	1,3-Dichlorobenzene	47.8	16.9	21.9
	1,4-Dichloorbenzene	41.8	14.9	19.4
	Ethylbenzene	48.5	27.2	22.8
	Toluene	90.5	30.0	28.4
	Average of all analytes	61.8	27.0	24.2
Wastewater 3	Benzene	45.4	26.5	23.2
	Chlorobenzene	50.5	20.5	13.6
	1,2-Dichlorobenzene	46.5	18.1	18.2
	1,3-Dichlorobenzene	33.0	15.3	17.9
	1,4-Dichloorbenzene	30.5	12.2	16.4
	Ethylbenzene	47.4	24.3	17.9
	Toluene	69.9	24.1	20.2
	Average of all analytes	46.2	20.1	18.2
	Grand Average	44.4	21.1	21.4

TABLE 22. SUMMARY OF PRECISION (% RSD-SA) BY ANALYTE, WATER TYPE, AND CONCENTRATION LEVEL

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Distilled water	Benzene	29.2	7.9	12.2
	Chlorobenzene	18.3	8.7	9.7
	1,2-Dichlorobenzene	15.7	18.6	15.7
	1,3-Dichlorobenzene	10.9	18.4	11.7
	1,4-Dichloorbenzene	27.3	18.0	13.4
	Ethylbenzene	33.7	26.1	9.6
	Toluene	25.6	8.7	10.9
	Average of all analytes	23.0	15.2	11.9
Tap water	Benzene	9.0	13.6	8.2
	Chlorobenzene	14.7	13.3	7.1
	1,2-Dichlorobenzene	25.6	8.8	12.0
	1,3-Dichlorobenzene	21.0	8.6	8.3
	1,4-Dichloorbenzene	24.0	9.6	9.2
	Ethylbenzene	16.8	10.9	10.3
	Toluene	17.0	12.6	8.1
	Average of all analytes	18.3	11.0	9.0
Surface water	Benzene	14.7	8.2	9.1
	Chlorobenzene	14.4	7.8	8.3
	1,2-Dichlorobenzene	11.2	8.6	11.0
	1,3-Dichlorobenzene	10.9	9.8	10.9
	1,4-Dichloorbenzene	9.4	12.0	11.1
	Ethylbenzene	20.4	8.2	7.8
	Toluene	15.9	7.8	9.2
	Average of all analytes	13.8	8.9	9.6

(continued)

TABLE 22 (continued)

Water type	Analyte	Low Youden pair	Medium Youden pair	High Youden pair
Wastewater 1	Benzene	36.1	12.1	14.5
	Chlorobenzene	70.7	13.0	10.2
	1,2-Dichlorobenzene	43.5	11.1	12.3
	1,3-Dichlorobenzene	20.9	19.2	11.6
	1,4-Dichloorbenzene	37.2	6.1	10.6
	Ethylbenzene	26.1	13.8	11.9
	Toluene	44.3	13.2	11.6
	Average of all analytes	39.8	12.6	11.8
Wastewater 2	Benzene	43.8	11.0	10.0
	Chlorobenzene	83.3	32.5	15.6
	1,2-Dichlorobenzene	38.7	11.8	10.5
	1,3-Dichlorobenzene	28.8	7.6	12.9
	1,4-Dichloorbenzene	38.5	11.0	11.0
	Ethylbenzene	30.1	12.0	10.7
	Toluene	54.5	31.8	13.4
	Average of all analytes	45.4	16.8	12.0
Wastewater 3	Benzene	24.1	11.3	8.9
	Chlorobenzene	28.1	12.0	9.9
	1,2-Dichlorobenzene	21.8	17.6	12.0
	1,3-Dichlorobenzene	22.8	12.9	11.3
	1,4-Dichloorbenzene	22.7	9.6	9.7
	Ethylbenzene	31.4	17.3	10.3
	Toluene	46.5	14.0	8.9
	Average of all analytes	28.2	13.5	10.1
	Grand Average	28.1	13.0	10.1

TABLE 23. RELATIVE MAGNITUDE OF INTERCEPTS IN THE LINEAR REGRESSION EQUATIONS

	Benzene		Chlorobenzene		1,2-Dichlorobenzene		1,3-Dichlorobenzene	
	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value
Distilled water								
$\bar{X}$	168	0.34	174	0.01	175	0.30	169	0.02
S	39.0	1.44	26.7	0.37	38.9	1.36	30.1	0.30
SR	20.6	2.86	16.8	1.37	27.9	0.14	21.0	0.48
Tap water								
$\bar{X}$	174	0.49	167	0.07	161	0.27	164	0.13
S	43.5	2.55	28.6	1.26	36.3	0.77	28.5	1.16
SR	15.2	0.40	13.0	0.92	20.0	2.10	13.8	2.40
Surface water								
$\bar{X}$	169	0.51	163	0.09	159	0.13	167	0.24
S	41.7	0.91	29.1	0.69	32.0	0.37	36.0	2.22
SR	15.3	1.11	13.5	1.04	17.2	0.23	18.1	0.06

(continued)

TABLE 23 (continued)

	Benzene		Chlorobenzene		1,2-Dichlorobenzene		1,3-Dichlorobenzene	
	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value
Wastewater 1								
$\bar{X}$	169	0.04	169	1.10[a]	164	0.23	171	1.96[a]
S	40.7	1.70	30.6	7.60[b]	45.9	1.03	48.2	1.72
SR	24.3	2.30	18.6	16.3[c]	20.2	4.60	21.2	2.17
Wastewater 2								
$\bar{X}$	162	0.22	169	11.7[a]	180	0.38	172	0.29
S	48.2	2.01	54.9	21.5[b]	35.8	3.13	37.1	2.13
SR	16.7	5.81[c]	33.8	43.9[c]	19.4	4.64	21.6	2.40
Wastewater 3								
$\bar{X}$	174	0.29	167	0.09	164	0.24	168	0.10
S	41.2	1.41	24.3	3.51	30.0	1.70	29.5	1.46
SR	15.9	3.64	17.0	2.53	20.5	0.68	19.3	1.51

(continued)

TABLE 23 (continued)

	1,4-Dichlorbenzene		Ethylbenzene		Toluene	
	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value
Distilled water						
$\bar{X}$	166	0.05	166	0.19	177	0.37
S	33.9	1.21	37.7	0.61	38.5	1.98
SR	23.2	1.25	18.9	2.44	19.0	2.53
Tap water						
$\bar{X}$	160	0.16	170	0.24	167	0.10
S	29.1	1.34	36.0	1.89	38.4	0.42
SR	14.9	2.62	17.6	1.02	14.4	1.25
Surface water						
$\bar{X}$	154	0.18	164	0.12	169	0.01
S	31.9	2.66	36.7	0.98	38.2	0.86
SR	17.2	0.35	13.0	2.54	19.4	1.17

(continued)

TABLE 23 (continued)

	1,4-Dichlorbenzene		Ethylbenzene		Toluene	
	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value	Average value	Intercept as percent of average value
Wastewater 1						
$\bar{X}$	162	0.33	167	0.23	162	0.61
S	32.0	1.84	35.0	1.14	43.3	1.55
SR	16.6	5.11[c]	20.4	1.87	19.4	5.40[c]
Wastewater 2						
$\bar{X}$	169	0.20	157	0.09	169	5.12[a]
S	32.1	1.53	36.9	1.44	50.5	8.63[b]
SR	18.9	4.50	17.2	2.62	26.8	13.0[c]
Wastewater 3						
$\bar{X}$	163	0.07	168	0.44	171	0.59
S	26.0	1.27	31.3	2.50	35.5	4.36
SR	15.9	2.14	18.6	2.80	16.4	7.33[c]

[a] Intercepts exceed 1 percent of average $\bar{X}$.

[b] Intercepts exceed 5 percent of S.

[c] Intercepts exceed 5 percent of SR.

Table 24 presents a comparison of the accuracy and precision (single analyst) obtained in this interlaboratory study versus those values reported by EPA in the description of the Test Method (Appendix A).

TABLE 24. COMPARISON OF SINGLE OPERATOR ACCURACY AND PRECISION

Analyte	Average percent recovery		Percent standard deviation	
	EPA[a]	This Study[b]	EPA[a]	This Study[b]
Benzene	91	92	10.0	10.0
Chlorobenzene	97	88	9.4	9.0
1,2-Dichlorobenzene	104	91	27.7	12.2
1,3-Dichlorobenzene	97	95	20.0	10.0
1,4-Dichlorobenzene	120	91	20.4	10.3
Ethylbenzene	98	92	12.4	11.8
Toluene	77	88	12.1	10.5

[a] Average of three matrix types (Table 2 - Appendix A).
[b] Average of six matrix types (Table 1 - this report).

In all cases except for toluene this study reports lower accuracies than the original EPA results. The single operator precision values for this study are equal or better than the EPA figures (lower % standard deviation).

EFFECTS OF WATER TYPES

The comparison of accuracy and precision across water types is summarized in Table 25, where the observed F values and the probability of exceeding the F values are entered for each of the seven analytes.

For every analyte except ethylbenzene and 1,4-dichlorobenzene, the F-test suggests a statistically significant effect due to water type (P[F>observed F]<0.05). The null hypothesis test indicates

TABLE 25. SUMMARY OF THE TESTS FOR DIFFERENCE ACROSS WATER TYPES

Compound	Observed F-value	P[F >observed F]	F test statistically significant at the 5% level	Statistical significance established by the 95% confidence limit	Waters	Practical significance established by the 95% confidence limit	Waters
Benzene	3.87	0.000	Yes	Yes	4, 5	No	-
Chlorobenzene	10.03	0.000	Yes	Yes	5	Yes	5
1,2-Dichlorobenzene	4.41	0.000	Yes	Yes	6	No	-
1,3-Dichlorobenzene	4.61	0.000	Yes	Yes	4	No	-
1,4-Dichlorobenzene	1.49	0.138	No	-	-	-	-
Ethylbenzene	1.83	0.053	No	-	-	-	-
Toluene	5.13	0.000	Yes	Yes	5	Yes	5

that a statistically significant effect has been established at the 95% confidence limit for the following analyte - water combinations: benzene in waters 4 and 5; chlorobenzene in water 5; 1,2-dichlorobenzene in water 6; 1,3-dichlorobenzene in water 4; and toluene in water 5. These effects are indicated since zero is not contained within the confidence limits for $(\ell n\ \beta_j - \ell n \beta_1)$ for the above analyte-water combinations.

The practical significance of these effects was determined by applying equations (21) and (22). In this case, a practical significance was established for only two cases: that of chlorobenzene and toluene in wastewater 5. These analyte-water combinations coincide with those which exhibited abnormally low slopes in the regression equations presented earlier in Table 1.

RESPONSES TO QUESTIONNAIRE

A Method 602 questionnaire was provided to all participating laboratories. Ten of twenty laboratories completed the questionnaire. Table 26 summarizes the analytical conditions employed by the responding laboratories. As shown in Table 26, laboratories 4 and 6 used SP-2100 rather than SP-1200 in their column packaging; in addition, all but four of the reporting laboratories used Tenax GC® only as the trap material. Omission of the OV-1 material specified by Method 602 could have adversely affected the precision of benzene and toluene analyses due to poorer desorption profiles. Laboratory 1 reported that negative peaks were caused by water when a Tenax/silica gel trap was employed; elimination of the silica gel cured this problem. Only three of the laboratories used a post-purge drying cycle. Laboratory 19 encountered some difficulties in using the drying cycle, but reported no problems when it was omitted.

TABLE 26. LABORATORY ANALYTICAL CONDITIONS

Laboratory code	Gas chromatogram	Temperature program, °C	Carrier gas/ flow rate, mL/min	Column packing	Column size
1	H-P 5880A	50°-2 min 6°/min to 90°	N_2/40	5% SP-1200/ 1.75% Bentone 34	-
3[a]	Tracor 700A	-	-	-	-
4	5711	50°-2 min 4°/min to 90°	He/36.8	5% SP-2100/ 1.75% Bentone 34	6' x 1/8" O.D. stainless
5	PE Sigma I	50°-6 min 30/min to 90°	He/20	5% SP-1200/ 1.75% Bentone 34	6' x 2 mm I.D. glass
6	H-P 5750	50°-2 min 6°/min to 90°	He/40	5% SP-2100/ 1.75% Bentone 34	6' x 1/8" stainless
7	PE 900	50°-2 min 6°/min to 90°	He/40	5% SP-1200/ 1.75% Bentone 34	6' x 0.085" I.D. stainless
8	Varian 37006C	50%-2 min 6°/min to 90°	He/40	5% SP-1200/ 1.75% Bentone 34	6' 2 mm I.D. glass
9[a]	PE 39206C	-	He	-	-
10[a]	-	-	-	-	-
11	Tracor 560A	50°-3 min 6°/min to 100°	He/30	5% SP-1200/ 1.75% Bentone 34	-
14	Fisher 2400	51°-2 min 8°/min to 93°	He/40	5% SP-1200/ 1.76% Bentone 34	6' x 1/8" stainless
17	H-P 5840	-	-	-	-
18	Microtech	50°-2 min 7.5°/min to 90°	He/20	5% SP-1200/ 1.75% Bentone 34	6' ? ? ? ?
19		50°-2 min 7.5%/min to 90°	He/20	5% SP-1200/ 1.75% Bentone 34	6' x 2 mm I.D. glass
20[a]	Tracor MT220	-	-	-	-

(continued)

TABLE 26 (continued)

Laboratory code	Detector temperature, °C	Lamp intensity	Purge/trap instrument	Mode	Purge, dry, desorb, bake cycle, min	Trap material
1	225	-	Tekmar LSC-2	Manual	P-12, DE-4, B-7	Tenax
3[a]	-	-	Takmar LSC-2		-	-
4	160	5	Tekmar LSC-1	Manual	P-12, D-6, DE-4, 13-7	Tenax
5	200	5	CDS 310	Manual	P-12, D-5, DE-7(Burn-180°C)	Tenax
6	250	7.5	Takmar LSC-2	Automatic	P-11, DE-7, B-4	50/50 Tenax, charcoal
7	230	5.5	Tekmar LSC-2	Automatic	P-12, D-6, DE-4, 13-15	Tenax
8	150	4			P-12, DE-4, B->7	Tenax
9[a]	-	-	Homemade	-	-	Tenax, OV-1, silicia gel, charcoal
10[a]	-	-	Tekmar	-	-	-
11	150	-	Homemade	Manual	P-12, DE-3, B-20	Tenax, 3% OV-1, silicia gel, charcoal
14	160	3	Homemade	Manual	P-12, DE-4, B-7	Tenax, 3% OV-1
17	-	-	Tekmar LSC-2	-	-	-
18	240	5	Tekmar	Manual	P-12, DE-4, B-10	Tenax
19	220	5	Tekmar LSC-2	Automatic	P-12, DE-5, B-35	Tenax
20[a]	-	-	Tekmar LSC-2	Automatic	-	-

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[a] Information from original proposed approach.

Nine of the ten responding laboratories reported no problems in the preparation of standards. Laboratory 6 stated that baseline drift at low concentration levels made them resort to manual quantitation of data. Eight of the laboratories reported no problems encountered in detection limits for the volatile aromatics. One of the laboratories reported poor detector sensitivity and the need for frequent lamp replacement. Laboratory 19 had difficulty detecting the lowest concentrations of 1,2-dichlorobenzene. As regards the linearity of detector response, seven of the responding laboratories observed good linearity over the entire concentration range. Laboratory 1 reported excellent linearity up to 50 µg/L. Laboratory 19 encountered problems at high concentrations because the upper limit of the integrator had reached its capacity. Laboratory 5 reported erratic results at low concentrations and observed poor linearity for toluene.

A wide variety of calibration methods were reported by the responding laboratories. These ranged from employing five concentrations of external standards plus a blank to running one near point concentration. Seven of the responding laboratories reported no problems in day-to-day variation in detector sensitivity. Three laboratories that did find variations attributed this to either changes in flow rate (Laboratory 6) or to clouding up of the detector lamp and the need for frequent cleaning (Laboratories 1 and 5). Laboratory 5 reported a 10%/day drop in sensitivity if the lamp was not cleaned.

Seven of the responding laboratories stated that no particular compound presented more problems than others. As mentioned above, Laboratory 19 had sensitivity problems for low concentrations of 1,2-dichlorobenzene. Laboratory 5 felt that laboratory air interferences and contamination of water matrices resulted in more problems in analyses of benzene compared to the other volatile aromatics. Laboratory 14 which employed a "homemade" purge/trap unit experienced carry-over problems with all the compounds when concentrations exceeded 50 µg/L.

Four of the responding laboratories reported no problems related to water types employed in the study. The other six laboratories experienced problems with the high background concentration of the volatile aromatics and other contaminants in the wastewaters. This was especially evident with wastewater 2 (water 5) where interfering peaks caused quantitation problems for low levels of toluene and the chlorobenzenes. The high levels of contaminants required the running of more blanks to check for carry-over from the purge/trap device.

In the category of miscellaneous comments and recommended improvements in Method 602, Laboratory 5 suggested a more detailed method for preparation of distilled water to avoid contamination due to laboratory air impurities. This method involves boiling water for 30 minutes, filling a 100-mL Erlenmeyer flask above the mark with boiling water, rapidly cooling in an ice bath, and immediately spiking and analyzing the resultant solution. Another criticism of the current procedure was the necessity of replacing the HNU detector lamp every one to two months (Laboratory 1). A long-lived lamp would alleviate this expensive problem. Laboratory 19 recommended omission of the post-purge drying step from the purge/trap cycle.

OTHER MONSANTO COMPANY FINDINGS DURING PRELIMINARY STUDIES

Some of the problems encountered by Monsanto Company during the preliminary studies and their potential solutions are presented below:

(1) Initial checkout of the HP 7675A purge/trap sampler showed random ghost peaks during the purge of

distilled water. Steam cleaning of the purge path seemed to alleviate the problem. This was accomplished during the purge mode by heating distilled water to boiling. The heating was continued for five minutes after steam became visible at the vent.

(2) The metal injection port (direct injection mode) was found to affect all dichlorobenzene area counts. Low counts for these compounds were corrected through the use of a glass liner packed with glass wool.

(3) Organic-free water blanks were needed after the analysis of wastewaters having water soluble materials and purgeable compounds that did not elute during standard program. It also was necessary to increase the column temperature for these blank runs.

(4) Detector quenching and gradual loss of response were two major problems. The quenching was minimized by increasing the post-purge time. However, the longer time almost doubled the purge volume. This may have caused another problem of analyte loss due to partial breakthrough. A possible example of this was noted in the 1000 x the minimum detectable level of the analytical curve. Comparisons of direct injection vs. purge/trap showed the greatest deviation of the diverging lines for benzene. The deviation became smaller through 1,2-dichlorobenzene where it was a near match. EPA in-house experience suggests that detector fouling could be caused by heating the column in excess of the 90°C temperature specified by Method 602 and venting through the detector.

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APPENDIX A

PURGEABLE AROMATICS

METHOD 602

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development EPA-600/4-82-057 July 1982

EPA

Test Method

Purgeable Aromatics—
Method 602

1. Scope and Application

1.1 This method covers the determination of various purgeable aromatics. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Benzene	34030	71-43-2
Chlorobenzene	34301	108-90-7
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
Ethylbenzene	34371	100-41-4
Toluene	34010	108-88-3

1.2 This is a purge and trap gas chromatographic method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 624 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above.

1.3 The method detection limit (MDL, defined in Section 12.1(1)) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from these listed depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval for alternate test procedures under 40 CFR 136.4 and 136.5

1.5 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a specially-designed purging chamber at ambient temperature. The aromatics are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the aromatics are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the aromatics onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the aromatics which are then detected with a photoionization detector[2,3].

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from interferences that may occur.

3. Interferences

3.1 Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high aromatic levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in an oven at 105 °C between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[4-6] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene and 1,4-dichlorobenzene. Primary standards of these toxic compounds should be prepared in a hood. An NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with hole in center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C for one hour before use.

5.2 Purge and trap device—The purge and trap device consists of three separate pieces of equipment: the sample purger, trap, and the desorber. Several complete devices are now commercially available.

5.2.1 The sample purger must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch.

5.2.2.1 The trap is packed with 1 cm of methyl silicone and 23 cm 2,6-diphenylene oxide polymer as shown in Figure 2. This trap was used to develop the method performance statements in Section 12.

5.2.2.2 Alternatively, either of the two traps described in Method 601 may be used, although water vapor will preclude the measurement of low concentrations of benzene.

5.2.3 The desorber must be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 200 °C. The desorber design, illustrated in Figure 2, meets these criteria.

5.2.4 The purge and trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3, 4, and 5.

5.3 Gas chromatograph—Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and stripchart recorder. A data system is recommended for measuring peak areas.

5.3.1 Column 1—6 ft long × 0.082 in ID stainless steel or glass, packed with 5% SP-1200 and 1.75% Bentone-34 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements and the MDLs listed in Tables 1 and 2. Guidelines for the use of alternate column packings are provided in Section 10.1.

5.3.2 Column 2—8 ft long × 0.1 in ID stainless steel or glass, packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on Chromosorb W-AW (60/80 mesh) or equivalent.

5.3.3 Detector—Photoionization detector (h-nu Systems, Inc. Model PI-51-02 or equivalent). This type of detector has been proven effective in the analysis of wastewaters for the parameters listed in the scope, and was used to develop the performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.1.

5.4 Syringes—5-mL glass hypodermic with Luerlok tip (two each), if applicable to the purge device.

5.5 Micro syringes—25 μL, 0.006 in ID needle.

5.6 Syringe valve—2-way, with Luer ends (three each).

5.7 Bottle—15-mL screw-cap with Teflon cap liner.

5.8 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. (Filtrasorb-300 or equivalent (Calgon Corp.)).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Hydrochloric acid (1 + 1)—Add 50 mL of concentrated HCl to 50 mL of reagent water.

6.4 Trap Materials

6.4.1 2,6-Diphenylene oxide polymer-Tenax, (60/80 mesh) chromatographic grade or equivalent.

6.4.2 Methyl silicone—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.5 Methyl alcohol—Pesticide quality or equivalent.

6.6 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids. Because benzene and 1,4-dichlorobenzene are suspected carcinogens, primary dilutions of these materials should be prepared in a hood.

6.6.1 Place about 9.8 mL of methyl alcohol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.6.2 Using a 100-μL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

6.6.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used, at any concentration, if they are certified by the manufacturer or by an independent source.

6.6.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4 °C and protect from light.

6.6.5 All standards must be replaced after one month, or sooner if comparison with check standards indicate a problem.

6.7 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sections 7.3.1 or 7.4.1 will bracket the working range of the analytical system. Secondary solution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards that can be used to determine the accuracy of calibration standards will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, in Cincinnati, Ohio.

7. Calibration

7.1 Assemble a purge and trap device that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Prior to use, daily condition traps 10 minutes while backflushing at 180 °C.

7.2 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those in Table 1. Calibrate the purge and trap-gas chromatographic system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4.).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 μL of one or more secondary dilution standards to 100, 500, or 1000 mL of reagent water. A 25-μL syringe with a 0.006 inch ID needle should be used for this operation. One of the external standards should be at a concentration near, but above, the MDL (see Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.3.2 Analyze each calibration standard according to Section 10, and tabulate peak height or area responses versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.4 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compound, α,α,α-trifluorotoluene, recommended as a surrogate spiking compound in Section 8.7 has been used successfully as an internal standard.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.6 and 6.7. It is recommended that the secondary dilution standard be prepared at a concentration of 15 μg/mL of each internal standard compound. The addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μg/L.

7.4.3 Analyze each calibration standard, according to Section 10, adding 10 μL of internal standard spiking solution directly to the syringe as indicated in Section 10.4. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using equation 1.

$$\text{Eq. 1 } RF = (A_sC_{is})/(A_{is}C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant ($<$10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.4.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate in methyl alcohol 500 times more concentrated than the selected concentrations. Quality control check sample concentrates, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8.2.2 Using a syringe, add 10 μL of the check sample concentrate to each of a minimum of four 5-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using Table 2, note the average recovery (X) and standard deviation (p) expected for each method parameter. Compare these to the calculated values for R and s. If $s > 2p$ or $|X - R| > 2p$, review potential problem areas and repeat the test.

8.2.5 The U.S. Environmental Protection Agency plans to establish performance criteria for R and s based upon the results of interlaboratory testing. When they become available, these criteria must be met before any samples may be analyzed.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R − 3s

where R and s are calculated as in Section 8.2.3

The UCL and LCL can be used to construct control charts(7) that are useful in observing trends in performance. The control limits above must be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly(7).

8.4 The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 11.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Each day, the analyst must demonstrate through the analysis of reagent water, that interferences from the analytical system are under control.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and blank with surrogate compounds (e.g. α,α,α,-trifluorotoluene). From stock standard solutions prepared as above, add a volume to give 7500 μg of each surrogate to 45 mL of organic-free water contained in a 50-mL volumetric flask, mix and dilute to volume (15 ng/μL). If the internal standard calibration procedure is being used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 7.4.2). Dose 10 μL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. Prepare a fresh surrogate spiking solution on a weekly basis.

9. Sample Collection, Preservation, and Handling

9.1 The samples must be iced or refrigerated from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site. USEPA Methods 330.4 or 330.5 may be used to measure residual chlorine(8). Field Test Kits are available for this purpose.

9.2 Collect about 500 mL sample in a clean container. Adjust the pH of the sample to about 2 by adding 1 + 1 HCl while stirring gently. Fill the sample bottle in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 All samples must be analyzed within 14 days of collection.(3)

10. Sample Extraction and Gas Chromatography

10.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and method detection limits that can be achieved by this method. An example of the separations achieved by Column 1 is shown in Figure 6. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

10.2 Calibrate the system daily as described in Section 7.

10.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

10.4 Allow sample to come to ambient temperature prior to introducing it into the syringe. Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 μL of the surrogate spiking solution (Section 8.7) and 10.0 μL of the internal standard spiking solution (Section 7.4.2), if applicable, through the valve bore, then close the valve.

10.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

10.6 Close both valves and purge the sample for 12.0 ± 0.1 minutes at ambient temperature.

10.7 After the 12-minute purge time, disconnect the purge chamber from the trap. Dry the trap by maintaining a flow of 40 mL/min of dry purge gas through it for six minutes. See Figure 4. A dry purger should be inserted into the device to minimize moisture in the gas. Attach the trap to the chromatograph, adjust the device to the desorb mode, and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180 °C while backflushing the trap with an inert gas between 20 and 60 mL/min for four minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30 °C (subambient temperature, if poor peak geometry and random retention time problems persist) instead of the initial program temperature of 50 °C.

10.8 While the trap is being desorbed onto the GC column, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

10.9 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180 °C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

10.10 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.11 If the response for the peak exceeds the working range of the system, prepare a dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

11. Calculations

11.1 Determine the concentration of individual compounds in the sample.

11.1.1 If the external standard calibration procedure is used, calculate the concentration of material from the peak response using the calibration curve or calibration factor determined in Section 7.3.2.

11.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.3 and equation 2.

Eq. 2.

$$\text{Concentration } \mu g/L = (A_s C_{is})/(A_{is})(RF)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

11.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

11.3 For samples processed as part of a set where the spiked sample recovery falls outside of the control limits which were described in Section 8.3, data for the affected parameters must be labeled as suspect.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero(1). The MDL concentrations listed in Table 1 were obtained using reagent water(9). Similar results were achieved using representative wastewaters.

12.2 This method has been demonstrated to be applicable for the concentration range from the MDL up to 1000 × MDL(9). Direct aqueous injection techniques should be used to measure concentration levels above 1000 × MDL.

12.3 In a single laboratory (Monsanto Research), using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained(9). The standard deviation of the measurement in percent recovery is also included in Table 2.

12.4 The Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

References

1. See Appendix A.
2. Bellar, T.A., and Lichtenberg, J.J. *Journal American Water Works Association, 66,* 739, (1974).
3. Bellar, T.A., and Lichtenberg, J.J. "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compunds," Proceedings of Symposium on Measurement of Organic Pollutants in Water and Wastewater. American Society for Testing and Materials, STP 686, C.E. Van Hall, editor, 1978.
4. "Carcinogens—Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.
5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised January 1976).
6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Safety, 3rd Edition, 1979.
7. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. March 1979.
8. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. March 1979.
9. "EPA Method Validation Study 24, Method 602 (Purgeable Aromatics)," Report for EPA Contract 68-03-2856 (In preparation).

Table 1. *Chromatographic Conditions and Method Detection Limits*

Parameter	*Retention Time (min.)*		*Method Detection Limit*
	Column 1	*Column 2*	*µg/L*
Benzene	*3.33*	*2.75*	*0.2*
Toluene	*5.75*	*4.25*	*0.2*
Ethylbenzene	*8.25*	*6.25*	*0.2*
Chlorobenzene	*9.17*	*8.02*	*0.2*
1,4-Dichlorobenzene	*16.8*	*16.2*	*0.3*
1,3-Dichlorobenzene	*18.2*	*15.0*	*0.4*
1,2-Dichlorobenzene	*25.9*	*19.4*	*0.4*

Column 1 conditions: Supelcoport 100/120 mesh coated with 5% SP-1200 and 1.75% Bentone-34 packed in a 6 ft. × 0.085 in ID stainless steel column with helium carrier gas at 36 cc/min flow rate. Column temperature held at 50°C for 2 min. then programmed at 6°C/min to 90°C for a final hold.

Column 2 conditions: Chromosorb W-AW 60/80 mesh coated with 5% 1,2,3-Tris(2-cyanoethyoxy)propane packed in a 6 ft. × 0.085 in ID stainless steel column with helium carrier gas at 30 cc/min flow rate. Column temperature held at 40°C for 2 min then programmed at 2°C/min to 100°C for a final hold.

Table 2. *Single Operator Accuracy and Precision*

Parameter	*Average Percent Recovery*	*Standard Deviation %*	*Spike Range (µg/L)*	*Number of Analyses*	*Matrix Types*
Benzene	*91*	*10.0*	*0.5-9.7*	*21*	*3*
Chlorobenzene	*97*	*9.4*	*0.5-100*	*21*	*3*
1,2-Dichlorobenzene	*104*	*27.7*	*0.5-10.0*	*21*	*3*
1,3-Dichlorobenzene	*97*	*20.0*	*0.5-4.8*	*21*	*3*
1,4-Dichlorobenzene	*120*	*20.4*	*0.5-10.0*	*21*	*3*
Ethylbenzene	*98*	*12.4*	*0.5-9.9*	*21*	*3*
Toluene	*77*	*12.1*	*0.5-100*	*21*	*3*

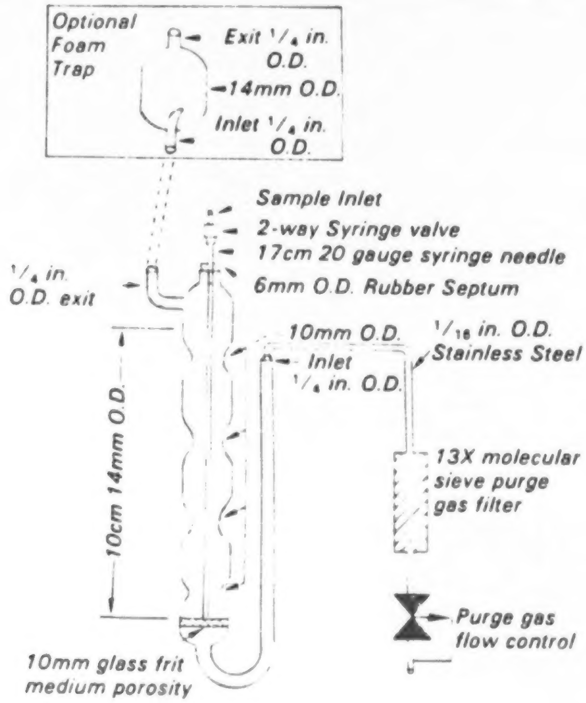
Optional Foam Trap
Exit 1/4 in. O.D.
14mm O.D.
Inlet 1/4 in. O.D.
Sample Inlet
2-way Syringe valve
17cm 20 gauge syringe needle
6mm O.D. Rubber Septum
1/4 in. O.D. exit
10mm O.D.
1/16 in. O.D. Stainless Steel
Inlet 1/4 in. O.D.
10cm 14mm O.D.
13X molecular sieve purge gas filter
Purge gas flow control
10mm glass frit medium porosity

Figure 1. *Purging device*

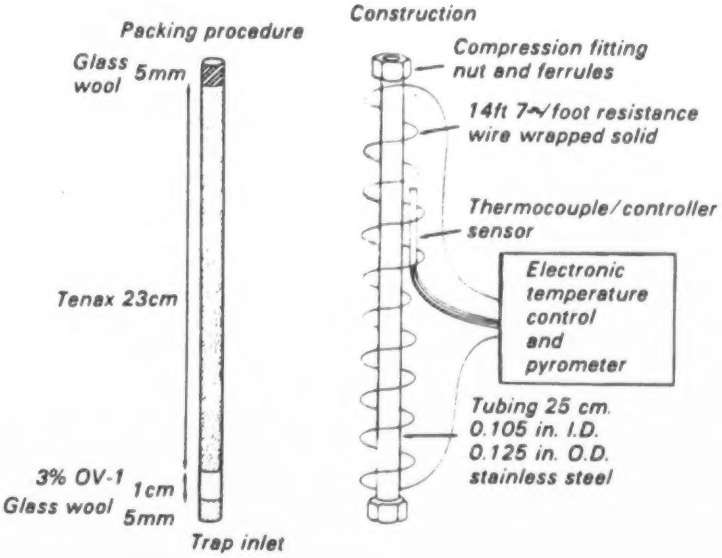
Packing procedure
Glass wool 5mm
Tenax 23cm
3% OV-1 1cm
Glass wool 5mm
Trap inlet
Construction
Compression fitting nut and ferrules
14ft 7~/foot resistance wire wrapped solid
Thermocouple/controller sensor
Electronic temperature control and pyrometer
Tubing 25 cm. 0.105 in. I.D. 0.125 in. O.D. stainless steel

Figure 2. *Trap packings and construction to include desorb capability*

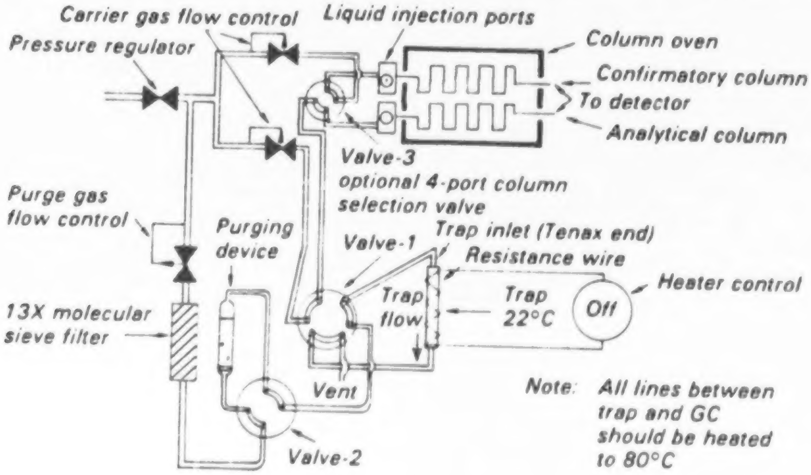
Carrier gas flow control
Liquid injection ports
Pressure regulator
Column oven
Confirmatory column
To detector
Analytical column
Valve-3
optional 4-port column selection valve
Purge gas flow control
Purging device
Valve-1
Trap inlet (Tenax end)
Resistance wire
Heater control
13X molecular sieve filter
Trap flow
Trap 22°C
Off
Vent
Valve-2
Note: All lines between trap and GC should be heated to 80°C

Figure 3. *Purge-trap system (Purge-sorb Mode)*

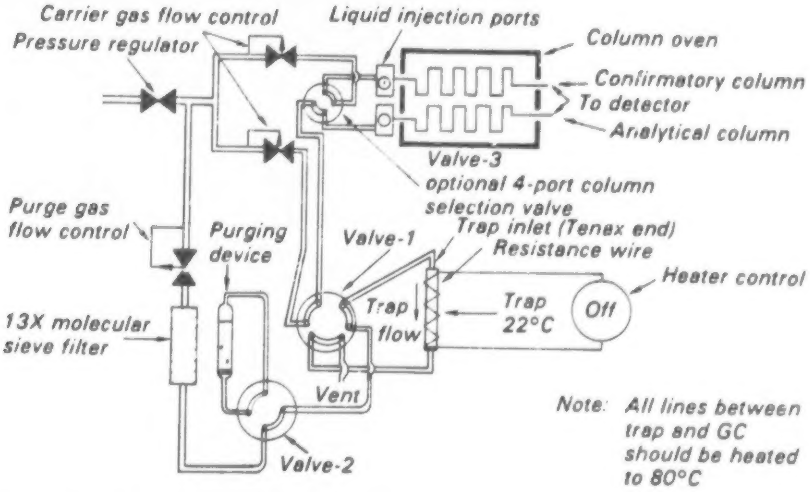
Carrier gas flow control
Liquid injection ports
Pressure regulator
Column oven
Confirmatory column
To detector
Analytical column
Valve-3
optional 4-port column selection valve
Purge gas flow control
Purging device
Valve-1
Trap inlet (Tenax end)
Resistance wire
Heater control
13X molecular sieve filter
Trap flow
Trap 22°C
Off
Vent
Valve-2
Note: All lines between trap and GC should be heated to 80°C

Figure 4. *Purge-trap system (Trap-dry Mode).*

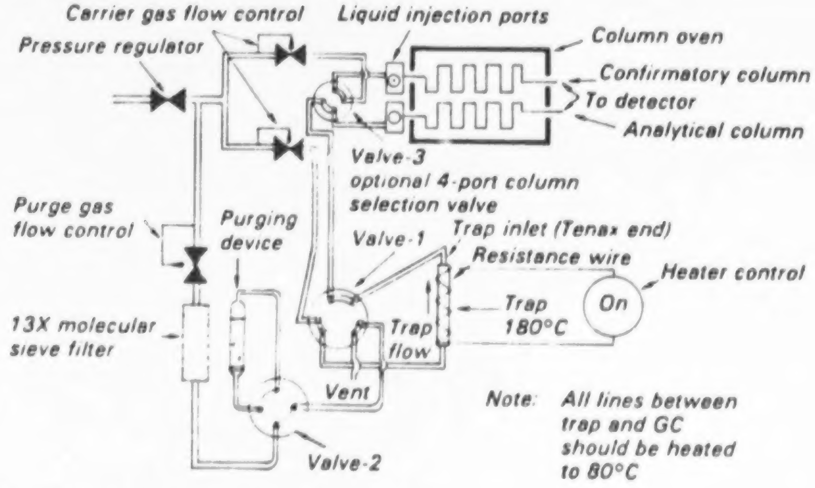
Carrier gas flow control
Liquid injection ports
Column oven
Pressure regulator
Confirmatory column
To detector
Analytical column
Valve-3
optional 4-port column
selection valve
Purge gas
flow control
Purging
device
Valve-1
Trap inlet (Tenax end)
Resistance wire
Heater control
On
Trap
180°C
13X molecular
sieve filter
Trap
flow
Vent
Valve-2
Note: All lines between
trap and GC
should be heated
to 80°C

Figure 5. *Purge-trap system (Desorb Mode).*

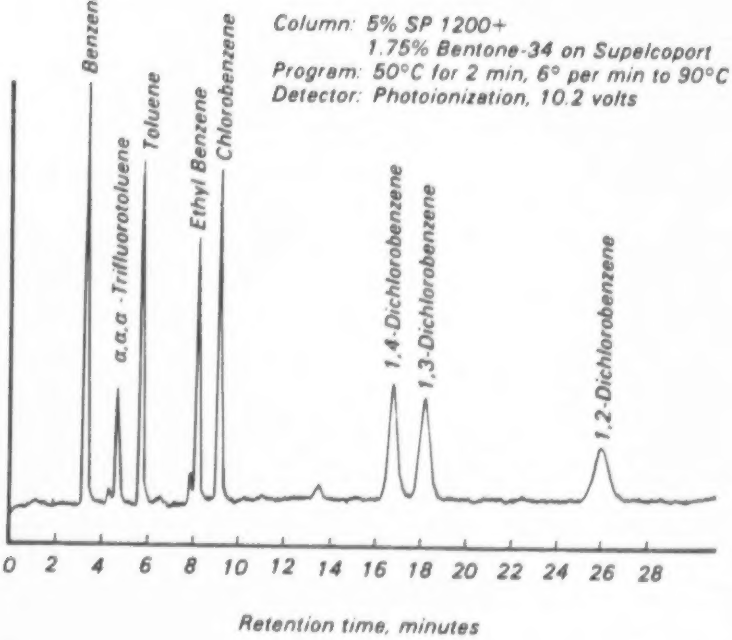

Figure 6. *Gas chromatogram of purgeable aromatics.*

APPENDIX B

ADDITIONAL NOTES ON METHOD 602

APPENDIX B

ADDITIONAL NOTES ON METHOD 602
(For Analysis Prestudy Conference Samples)

3.1* Steam cleaning of the purge path may help to rid system from a buildup of impurities. This can be accomplished during the purge mode by heating organic-free water in the purge vessel to boiling. The heating should continue for approximately 5 minutes after steam becomes visible at the purge vent.

3.3 Cross contamination can occur in two primary areas: the purge path and the analytical column. Suggestions listed in the 3 December 1978 Federal Register (Section 3.3) and the above steam cleaning method can be used for the purge path. (Steam cleaning should be used only if other methods fail.) It may become necessary to increase the analytical column temperature to 150°C after elution of the last analyte in order to eliminate a buildup of high boiling compounds (wastewaters).

Caution: The upper limit for Bentone-34 is 180°C. (See note in Section 8.5 of these notes, regarding loss of PID sensitivity.)

5.2 Appropriate purge/trap samplers are those such as the Hewlett-Packard with up to a 15-mL purging vessel or the Tekmar with 5-mL purging vessel. Do not use Tekmar with a 25-mL purging vessel.

NOTE: The preliminary investigation of Method 602 (see Appendic C) was conducted employing a Hewlett-Packard purge/trap device which does not meet the specifications stated in Method 602, Section 5.2.2 (see Appendix A).

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*Section numbers refer to sections in Method 602 description presented in Appendix A.

5.7 A 10- to 15-mL screw-cap is acceptable. We have found a 10-mL cap to be preferable.

6.2/9.1

Any sodium thiosulfate needed in the wastewater samples has already been added by MRC.

6.4/7.1

The general purpose trap containing 1.3 cc of Tenax G.C.® used in the Hewlett-Packard purge/trap sampler showed acceptable efficiency without the use of the small amount of 3% OV-1. Either trap is acceptable. (Note: The inclusion of OV-1 is to help improve the desorption of certain compounds. Deletion of this material can adversely affect the precision of benzene and toluene analyses.)

6.1.1

The organic-free water should be used as soon as possible after it has passed through the carbon filter bed. Trace impurities can be picked up from even a brief exposure to lab air. Try to minimize the number of transfers to other vessels and the time required for each transfer.

7.2/10.1

We have been informed that the column material cited in the Federal Register (Vol. 44) was a typing error. It should have read 5% SP-1200 instead of SP-2100.

NOTE: We have evaluated Method 602 using SP-2100. The SP-2100, however, appears to give a better resolution than the SP-1200. All compounds eluted from 1 min (benzene) to as much as 8 min

(1,2-DCB) earlier under the following conditions of analysis. (EPA cites xylene interferences as the reason for the choice of SP-1200.)

Column gas flow: Helium, 40 mL/min

Column: 6' x 0.085" I.D. SS packed with 5% SP-2100 and 1.75% Bentone-34 on Suppelcoport 100/120

Column program: 50°C for 2 min, programmed at 8°/min to 90°C, with a 16-min hold

7. Note: All standards and samples are to be analyzed by purge/trap. Determination of purging efficiency or recovery by direct injection is not required for this study. Method precision and sensitivity limits will be determined by multiple laboratory results and do not need to be determined by individual laboratories.

8.5 Standard quality assurance practices should be used. In the conduct of this work, it is recommended that a blank and a three point calibration curve be analyzed on the first day. On following days, a blank and one point should be sufficient if the point falls within 10% of the previously generated calibration curve.

NOTE: The photoionization detector will show a continual loss in response due to the deposition of high boiling compounds (including column bleed) onto the PID lamp window. (Window cleaning becomes necessary when MDLs cannot be achieved or when a significant decrease in sensitivities is noted.)

8.6 For the purpose of this study do not add surrogate compounds.

9.1 Samples should be refrigerated until analysis.

9.3 Delete (for Round-Robin Only)

10.0 Sample extraction and gas chromatography for users of the purge device shown in Figure 1 page 69477 of the Federal Register, Vol. 44, No. 233/12-3-79.

10.4 Delete last sentence concerning surrogates.

10.8 We recommend a minimum of three washes.

11.1 Refer to Section 7.2 of these notes.

10.2 No duplicate analyses are required for this study.

The Notes for Section 10.3 and 10.4 have been generated using a Hewlett-Packard 7675A P/T Sampler but also may be applicable for other P/T devices.

10.3 Keeping an empty purge vessel or one containing organic-free water on sampler when not in use may reduce contamination.

10.4 The purge vessel design is quite different from that described in Federal Register Method 602. The HP7675A uses a 15-mL threaded test tube as the purge vessel. The design allows one to change the vessel after each analysis thus minimizing cross contamination. Blanks, standards, and field-type samples can be introduced as per instructions listed in 9.2 of the Federal Register or by filling to the mark on a precalibrated purge vessel. All purge vessels should be sealed with a Teflon®-lined screw cap if not attached to sampler immediately after filling.

NOTE: Surrogates will not be used for Round-Robin Study.

10.5-10.9

HP7675-A P/T Samplers.

Attach the purge vessel containing 5 mL of sample to P/T sampler. Start the following automated or semi-automated sequence for analysis. The following conditions have been found to give good results:

TABLE 27. AUTOMATED (5830/40) GAS CHROMATOGRAPHS

Event	Time, min
Purge cycle	12
Post-purge cycle (pre-purge valve settings)	6
Desorb cycle	4
Vent cycle	7

Semi-Automated 7675A (Stand-Alone Version)

Initial set points are as follows:

TABLE 28. INITIAL SET POINTS

Event	Time, min
Pre-purge cycle	0
Purge cycle	13
Desorb cycle	4
Vent cycle	7

Attach purge vessel and press Start Run on the 7675A. Set a time of 6 min on Pre-Purge Cycle (this becomes "post purge" time after next step). At 12 minutes into run, press Stop Run followed by Start Run on 7675A sampler. (Unit should now be under Pre-Purge Timer.) During this Post-Purge Cycle, reduce Purge Time to zero (0). At the end of the six-minute "Post Purge", the sampler will automatically proceed through the desorb and vent cycles.

Upon completion of vent cycle, the trap is automatically cooled to make ready for the next sample (purge vessel).

Description of Events

Purge Cycle (12 min)

Volatiles are purged from sample onto the Tenax® trap which is at or below ambient.

Post-Purge Cycle (6 min)

Purge Vessel is switched out of system (flow path), and trap is dried by maintaining a 40-mL/min dry purge for 6 minutes.

Desorb Cycle (4 min)

Trapped materials are introduced to the G.C. Column by rapidly heating trap to 180°C while backflushing trap with an inert gas at 40 mL/min for 4 minutes.

Vent Cycle (7 min)

Trap is reconditioned by increasing trap temperatures by 50°C (to 230°C) while venting to atmosphere (hood).

10.1 Refer to Section 7.2 of these notes for comments.

11.2 No duplicate analyses are required for this study.

APPENDIX C

PRELIMINARY INVESTIGATION OF METHOD 602

APPENDIX C

PRELIMINARY INVESTIGATION OF METHOD 602

Before initiation of the interlaboratory study of EPA Method 602, Monanto Research Corporation (MRC) conducted an evaluation of the method. The objective of these preliminary studies was to develop a detailed knowledge of the Method 602 procedure before the 20 participating laboratories began their analysis effort. Any problems and solutions to problems could then be transmitted to the participating laboratories before their work was initiated. In addition, MRC would then be in a position to offer real assistance to these laboratories if they experienced difficulties during the method validation effort. The tasks in these preliminary studies included:

- An evaluation of Method 602, including shakedown runs of equipment and the total analytical procedure, purge efficiency.

- Stability studies of concentrated (spike) solutions of the seven aromatic compounds.

- A determination of Method Detection Limits (MDL) in interference-free water and two wastewaters.

- A determination of the analytical curves for analysis of the aromatic compounds.

- The preparation of a summary of problems encountered by MRC in the conduct of Method 602 and the development of recommended solutions to these problems.

In this investigation a Hewlett-packard purge/trap device was employed which does not meet the specifications for Method 602 (Appendix A).

The results of these preliminary studies are summarized below.

Evaluation of Method 602 - Purgeable Aromatics

Two sets of ampuls were prepared containing the seven aromatic compounds such that the spiked water would contain either 0.2 µg/L or 50 µg/L of each compound. Method 602 was run using these ampuls, and analyes of the concentrates were performed by direct injection chromatography for future comparison as a stability test. Any problems encountered in the conduct of the teste were noted.

Recovery studies comparing purge/trap results to direct injection of purgeable aromatics at the 5-µg/L level indicated purge efficiencies exceeding 90 percent for all compounds (average of 97.5 percent). Purge gas volumes were 480 mL with no post-purge time. Using post-purge cycle times of 6 and 10 minutes, the percent recovery fell to an average of 90 percent and 86 percent, respectively. The reduction of percent recovery is not necessarily related to poor purge efficiency, because a repurge of standard samples indicated residual content of all compounds to be less than 1 percent of the original purge values.

Stability Studies

Stability studies of the concentrated standards in the sealed ampuls were plagued by operational difficulties encountered with the HNU PHotoionization Detector (PID). The detector demonstrated a loss in sensitivity with time, and a new 10.2-eV UV lamp had to be obtained to complete the stablity studies. Despite these difficulties, the 79-day and 96-day stabilities of the sealed ampul standards appeared to be very acceptable.

Determination of Method Detection Limits (MDL)

The method detection limits (MDL) were determined according to Procedure A of Revision 1.7 EMSL-Ci, dated 1-15-80. Organic-free water and two different wastewaters were spiked and purged employing Method 602 with minor modifications. The resultant MDL values for these three waters are presented in Table 29.

TABLE 29. SUMMARY OF METHOD 602 DETECTION LIMIT DATA (μg/L)

compound	Organic-free water	Wastewater 1	Wastewater 2
Benzene	0.2	>1.0	>26
Chlorobenzene	0.2	0.2	>120
1,2-Dichlorobenzene	0.4	>24	>6.4
1,3-Dichlorobenzene	0.4	0.3	2.0
1,4-Dichlorobenzene	0.3	0.3	6.1
Ethylbenzene	0.2	0.2	>20
Toluene	0.2	2.2	>164

Determination of the Analytical Curves

The analytical curves of each of the seven purgeable aromatic compounds were determined by both Method 602 and direct injection chromatography employing solutions at approximately 4, 7, 10, and 100 times the minimum detection limits. Using both methods, excellent linearity was obtaned after plotting peak area counts versus concentration. For Method 602, the minimum correlation of slope and intercept was 0.9994 for a single aromatic compound.

APPENDIX D

ANALYSES OF STANDARD SPIKING SOLUTIONS EMPLOYED IN METHOD 602

APPENDIX D

ANALYSES OF STANDARD SPIKING SOLUTIONS EMPLOYED IN METHOD 602

The six concentrated purgeable aromatic standards shipped to the participating laboratories in sealed glass ampuls were analyzed by direct injection chromatography for each of the seven aromatic compounds. In each case, a Perkin-Elmer Model 3920 B chromatograph was employed with a flame ionization detector. Three different chromatographic columns were used: a Tenax® column for analysis of benzene and toluene in the low concentration Youden pair (solutions 1 and 2); a FFAP column for the remaining purgeable aromatics in the low concentration Youden pair; and a 5% SP-1200/5% Bentone-34 on 100/120 mesh Supelcoport column for analysis of all the purgeable aromatics in the intermediate (solutions 3 and 4) and high (solutions 5 and 6) Youden-pair standards. The instrumental conditions are summarized in Table 30.

The Tenax® column separated the methanol solvent from the aromatic compounds, but would not resolve the dichlorobenzene isomers. The FFAP column resolved the isomers without significant bleed, but the benzene and toluene peaks were lost in the methanol solvent peak.

The results of the analyses are presented in Table 31 in terms of the equivalent concentrations of the analytes in the water matrices after spiking with the ampul contents.

The mean recoveries generated from the regression equation by the twenty laboratories also support the statement that the ampul concentrations are correct.

TABLE 30. CHROMATOGRAPHIC CONDITIONS

Chromatograph:	Perkin-Elmer 3920B with flame ionization detector (FID)		
Columns:	6' x 1/4" stainless Tenax® 35-60 mesh	20' x 1/4" stainless FFAP	10" x 1/8" 5% SP1200/5% Bentone 34 on 100/120 mesh Supelcoport (stainless steel)
Temperatures:			
Column:	100-150°C by 4°C/min	60→135°C, hold for 4 min, then 4°C/min	90°C/8 min to 115°C/20 min by 32°C/min
Injection port:	250°C	250°C	250°C
Detector:	250°C	250°C	250°C
Carrier gas:	He at 30 mL/min	He at max. flow	He at 30 mL/min

TABLE 31. STABILITY DATA

Ampul	1		2		3		4		5		6	
	TV	AV	TV	AV	TV	AV	TV	AV	TV	AV	TV	AV
Benzene	2.2	2.5	3.0	3.1	46	44	54	53	450	330	550	444
Chlorobenzene	2.2	2.6	3.0	3.5	46	46	54	53	450	474	551	600
1,2-Dichlorobenzene	2.2	2.4	3.0	3.6	46	45	54	53	449	504	600	636
1,3-Dichlorobenzene	2.2	2.8	3.0	4.1	46	41	54	51	450	486	550	630
1,4-Dichlorobenzene	2.2	2.4	3.0	3.2	46	48	54	58	450	524	550	666
Ethylbenzene	2.2	2.3	3.0	3.0	46	38	54	44	452	404	551	600
Toluene	2.1	2.3	3.0	3.2	46	44	54	53	450	402	550	540

Note: TV = true value, µg/L; AV = analytical value, µg/L.

APPENDIX E

RAW DATA: METHOD 602

TABLE 32. RAW DATA FOR BENZENE ANALYSIS BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	2	1	2	1	2	1	2	1	2	1	2
TRUE CONC:	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
LAB NUMBER												
1	2.39	2.89	2.26	2.71	2.26	2.49	0.81	0.78	0.83	0.34	0.77*	0.75*
2	3.28	4.76	3.00	3.86	4.09	4.57	2.32	4.41	2.42	3.43	2.89	3.18
3	1.64	2.13	1.18	1.76	1.84	2.06	1.67	0.77	0.74	0.69	1.41	2.24
4	2.37	3.01	2.06	2.75	2.22	2.91	1.83	2.50	1.82	2.38	2.16	2.45
5	1.28	1.71	2.37	3.43	2.05	2.65	3.15	1.64	2.29	3.67	2.00	2.16
6	2.14	2.21	2.21	2.93	2.29	2.71	2.71	4.14	5.35	3.28	2.71	1.64
7	2.02	2.92	1.98	2.87	2.12	2.99	3.75	5.25	2.17	0.00*	1.91	3.14
8	1.36	1.88	1.57	2.03	1.52	1.92	2.54	2.66	1.97	3.24	1.60	2.24
9	6.55*	8.48	5.25	5.63	4.64	4.97	9.16*	3.78	0.00*	0.00*	0.00*	0.00*
10	2.02	2.79	2.07	3.10	2.09	2.71	2.26	0.48	3.02	3.06	3.32	5.05
11	1.91	2.95	2.20	2.28	1.74	3.53	1.00	1.11	1.38	2.08	1.33	0.00*
12	*	*	1.30	*	*	3.12*	*	*	5.20*	*	*	*
13	11.90*	13.90*	8.62	9.57*	1.37	14.70*	1.31	13.40*	19.00*	0.00*	8.95*	16.10*
14	2.58	4.07	5.38	5.96	3.48	3.58	1.10	3.25	0.86	1.55	4.61	5.30
15	2.10	6.62	3.28	2.80	71.00*	82.00*	0.00*	0.72	7.00*	4.13*	0.00*	0.00*
16	3.19	4.72	1.23*	1.60*	1.54*	0.00*	1.69	2.89	2.19	7.10	3.15	3.15
17	9.59*	12.10*	6.66	6.87	7.19*	8.27*	4.82	4.81	2.30	3.40	4.70	6.44
18	3.50	1.80	1.29	2.26	3.67	2.88	3.07	3.94	5.42	5.92	2.87	5.92
19	4.27	5.75	4.96	5.20	2.04	2.46	1.33	3.11	1.64	0.09	1.81	1.70
20	2.86	2.97	1.52	2.65	2.11	3.45	0.56	2.14	2.81	0.00*	1.38	2.63

TABLE 32 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
LAB NUMBER												
1	33.70	41.30	34.90	44.00	36.10	40.10	37.70	35.50	38.20	33.00	32.40*	42.20*
2	50.80	54.60	45.50	56.80	46.10	50.70	42.30	48.40	39.60	45.40	45.50	54.50
3	128.00*	111.00*	126.00*	127.00*	19.10*	20.70*	19.10	21.00	18.40*	20.00	18.20	21.50
4	43.10	52.70	46.00	53.50	47.10	55.10	46.60	54.80	41.80	53.00	47.80	54.50
5	46.40	48.60	44.70	66.00	37.10	43.30	47.40	53.00	41.50	47.90	40.60	44.10
6	40.00	42.00	40.50	48.40	40.00	48.90	42.10	50.00	44.70	55.80	41.60	48.90
7	41.70	52.20	41.30	49.00	45.30	51.30	49.20	56.20	38.60	44.10	43.80	53.00
8	43.30	41.00	47.20	39.80	50.10	44.30	49.20	43.40	45.00	42.00	45.10	39.60
9	49.20	58.30	53.40	63.40	53.00	56.20	51.50	52.30	49.00	55.80	61.90	68.00
10	48.70	51.00	46.30	53.00	51.70	58.90	56.50	44.60	56.00	47.40	50.60	52.00
11	45.40	40.10	55.00	41.10	46.70	41.30	36.20	33.80	40.00	41.60	40.00	31.30
12	163.00*	400.00*	150.00*	200.00*	169.00*	305.00*	150.00*	188.00*	188.00*	363.00*	104.00*	438.00*
13	125.00*	128.00*	81.00*	81.40	127.00*	124.00*	63.10	47.00	95.80*	23.70	121.00*	117.00*
14	44.80	51.00	47.90	51.70	44.80	51.40	50.80	50.10	45.00	42.40	44.10	53.40
15	48.00	63.20	57.20	68.60	159.00*	87.00*	54.40	62.90	64.30*	71.00*	68.50	64.30
16	35.70	37.20	34.40*	26.80*	33.00*	30.00*	24.70	37.50	33.10	25.40	25.70	45.90
17	94.30*	37.30	107.00*	77.00	55.60	56.60	51.00	46.70	41.90	39.00	49.30	57.00
18	58.60	61.10	60.30	62.70	52.70	56.80	62.90	74.20	49.40	56.10	51.90	65.60
19	41.60	46.10	37.70	65.10	35.80	53.20	29.50	36.20	35.00	39.90	30.10	35.10
20	33.10	42.20	34.70	49.00	41.70	46.70	19.10	21.50	48.70	59.70	44.00	39.10

TABLE 32 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	5	6	5	6	5	6	5	6	5	6	5	6
TRUE CONC:	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
LAB NUMBER												
1	335.00	402.00	250.00	354.00	289.00	353.00	519.00	348.00	317.00	363.00	256.00*	354.00*
2	516.00	555.00	557.00	627.00	496.00	639.00	405.00	668.00	453.00	643.00	513.00	639.00
3	609.00	695.00	676.00	718.00	638.00	816.00	592.00	595.00	636.00	732.00	567.00	666.00
4	440.00	538.00	439.00	538.00	448.00	548.00	411.00	537.00	457.00	551.00	448.00	535.00
5	476.00	460.00	399.00	446.00	412.00	540.00	425.00	468.00	434.00	601.00	431.00	532.00
6	324.00	404.00	387.00	393.00	362.00	389.00	392.00	419.00	379.00	393.00	370.00	393.00
7	436.00	544.00	417.00	542.00	424.00	522.00	364.00	538.00	406.00	493.00	436.00	539.00
8	578.00	516.00	596.00	528.00	543.00	527.00	561.00	524.00	549.00	536.00	605.00	503.00
9	244.00	276.00	228.00	283.00	244.00	250.00	333.00	361.00	322.00	403.00	342.00	401.00
10	476.00	548.00	456.00	602.00	382.00	552.00	466.00	567.00	448.00	578.00	401.00	524.00
11	364.00	452.00	362.00	443.00	365.00	448.00	374.00	459.00	354.00	427.00	358.00	422.00
12	1500.00*	1375.00*	2375.00*	1500.00*	2000.00*	1750.00*	1375.00*	1875.00*	1500.00*	1375.00*	1375.00*	1500.00*
13	741.00*	516.00*	378.00	400.00	625.00	644.00	315.00	303.00	136.00	100.00	771.00*	816.00*
14	470.00	557.00	458.00	570.00	455.00	546.00	486.00	497.00	512.00	598.00	476.00	605.00
15	528.00	596.00	640.00	795.00	723.00*	855.00*	618.00	783.00	675.00*	786.00*	661.00	801.00
16	402.00	398.00	292.00*	382.00*	281.00*	471.00*	457.00	434.00	388.00	583.00	331.00	380.00
17	347.00	279.00	436.00	468.00	306.00	330.00	287.00	310.00	229.00	262.00	312.00	332.00
18	464.00	631.00	410.00	481.00	382.00	467.00	427.00	546.00	470.00	562.00	399.00	485.00
19	375.00	429.00	327.00	369.00	414.00	451.00	326.00	385.00	279.00	382.00	373.00	409.00
20	227.00	497.00	386.00	476.00	365.00	374.00	427.00	512.00	433.00	499.00	379.00	499.00

TABLE 33. RAW DATA FOR CHLOROBENZENE ANALYSIS BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	2	1	2	1	2	1	2	1	2	1	2
TRUE CONC:	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
LAB NUMBER												
1	2.13	2.75	2.21	2.61	2.25	2.46	0.65	0.00*	0.00*	0.00*	1.72	1.50
2	2.11	3.62	1.75	2.52	2.72	3.60	0.30	7.40	3.00	11.00	0.91	1.25
3	2.08	2.64	1.75	2.54	1.51	2.52	0.60	0.00*	0.00*	0.00*	1.44	2.07
4	2.21	2.99	2.30	3.22	2.13	3.18	0.00*	0.00*	0.00*	0.00*	3.42	3.91
5	1.79	2.32	1.56	2.02	2.09	3.00	0.00*	0.91	0.00*	0.00*	2.32	2.63
6	2.62	2.62	1.69	2.62	1.69	2.46	2.46	3.07	0.00*	0.00*	1.80	0.00*
7	2.07	3.16	3.67	3.28	2.10	3.01	1.30	4.40	0.00*	0.00*	0.32	2.46
8	1.56	2.02	1.49	2.14	1.75	2.13	2.20	0.00*	38.00	0.00*	0.00*	2.90
9	6.34*	8.26*	4.10	6.78*	4.01*	6.26*	0.00*	0.00*	0.00*	0.00*	3.69	0.00*
10	2.11	2.73	2.36	3.60	2.45	2.51	2.30	0.00*	0.00*	2.00	4.80	8.90*
11	0.97	2.97	1.08	1.85	0.96	1.18	7.80	3.70	52.00	14.00	1.81	3.09
12	2.97	2.37	2.97*	3.66*	2.57*	3.37*	0.00*	0.00*	0.00*	0.00*	5.74*	6.34*
13	2.80	5.44*	1.62	1.95	1.49	1.82	0.00*	7.84	0.00*	0.00*	3.69	4.98
14	2.81	3.37	2.83	4.23	2.83	3.73	2.20	7.20	3.00	6.00	2.93	3.17
15	2.55	3.33	2.95	2.75	2.12	2.87	9.30*	11.30*	46.00*	59.00*	3.14*	3.96*
16	2.30	2.40	0.98*	0.82*	1.83	1.72	3.00	14.00	0.00*	35.00	2.05	1.52
17	9.90*	12.40*	16.60*	17.80*	13.70*	15.60*	8.70	14.20	21.00	37.00	5.10	3.10
18	1.89	1.36	2.59	3.08	1.32	0.81	0.00*	0.00*	0.00*	0.00*	0.65	1.21
19	2.41	2.68	1.81	2.51	1.51	2.03	0.60	0.00*	0.00*	0.00*	1.61	1.52
20	2.26	2.92	3.37	2.96	2.22	3.11	0.00*	0.00*	0.00*	0.00*	1.71	2.56

TABLE 33 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
LAB NUMBER												
1	41.10	44.50	34.60	46.20	34.80	41.90	71.20	52.00	77.70	32.70	45.10	56.50
2	45.20	50.90	39.90	52.00	40.20	47.50	41.10	49.90	23.00	27.00	49.80	44.70
3	86.70*	81.00	84.00*	89.50*	23.40	25.70	19.60	20.20	111.00	95.60	24.10	28.40
4	44.90	53.30	45.80	53.40	46.10	53.90	35.30	43.40	33.50	29.70	49.50	54.20
5	48.50	49.40	43.60	53.30	39.90	45.10	44.40	52.10	21.60	23.60	42.40	45.30
6	44.30	50.00	42.90	52.90	42.80	54.30	44.30	55.70	43.30	62.30	43.30	49.00
7	41.60	50.40	41.20	46.50	41.90	48.00	47.40	55.20	9.00	13.00	43.50	53.00
8	45.60	41.40	47.30	38.00	51.40	48.30	40.60	41.30	73.00	45.00	55.70	58.60
9	50.50	66.90	69.30	68.10	62.90	63.90	37.50	38.10	28.20	45.80	57.80	60.70
10	46.30	57.10	45.40	59.60	53.40	61.40	55.20	60.30	39.00	54.00	60.30	44.30
11	42.00	43.10	58.50	43.90	45.20	43.80	52.00	51.70	61.00	68.00	42.20	51.40
12	172.00*	182.00*	160.00*	186.00*	183.00*	196.00*	235.00*	263.00*	146.00	103.00	138.00*	141.00*
13	63.00	67.80	45.10	50.10	61.30	63.90	34.40	32.10	106.00	56.40	35.00	45.20
14	52.60	60.40	54.40	61.10	53.00	60.90	57.40	64.80	60.00	61.00	54.80	64.00
15	43.60	62.70	56.70	60.70	55.30	60.80	64.70*	73.20*	123.00*	118.00*	69.00*	62.40*
16	26.70	42.00	31.60*	21.40*	36.60	29.80	35.50	54.00	62.00	16.00	41.20	61.10
17	101.00*	42.80	103.00*	76.10*	91.60*	96.40*	48.70	44.90	27.00	14.00	36.80	40.30
18	36.20	38.80	54.20	50.20	45.90	55.30	44.50	38.50	0.00*	0.00*	47.30	65.60
19	40.80	44.70	37.60	61.30	37.60	52.40	28.00	28.60	38.00	43.00	31.70	36.30
20	43.80	51.10	39.30	51.00	46.00	49.70	31.80	37.00	30.00	29.00	42.60	42.70

TABLE 33 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	5	6	5	6	5	6	5	6	5	6	5	6
TRUE CONC:	450.00	551.00	450.00	551.00	450.00	551.00	450.00	551.00	450.00	551.00	450.00	551.00
LAB NUMBER												
1	366.00	438.00	298.00	406.00	312.00	384.00	476.00	533.00	667.00	581.00	416.00	469.00
2	414.00	451.00	435.00	503.00	398.00	504.00	341.00	485.00	353.00	548.00	395.00	486.00
3	522.00	551.00	502.00	559.00	481.00	571.00	494.00	540.00	307.00	340.00	458.00	537.00
4	446.00	545.00	443.00	546.00	452.00	560.00	406.00	533.00	461.00	545.00	452.00	543.00
5	438.00	516.00	392.00	468.00	418.00	505.00	399.00	460.00	421.00	501.00	414.00	509.00
6	400.00	400.00	434.00	400.00	400.00	391.00	451.00	436.00	429.00	376.00	406.00	410.00
7	437.00	545.00	416.00	538.00	402.00	518.00	360.00	527.00	368.00	454.00	436.00	539.00
8	894.00*	560.00	915.00*	544.00	863.00*	534.00	874.00*	627.00	823.00*	519.00	863.00*	578.00
9	323.00	354.00	296.00	360.00	274.00	327.00	311.00	348.00	289.00	424.00	487.00	473.00
10	469.00	508.00	470.00	568.00	369.00	418.00	489.00	496.00	424.00	471.00	390.00	452.00
11	375.00	485.00	404.00	499.00	401.00	504.00	419.00	513.00	424.00	498.00	406.00	490.00
12	1980.00*	1861.00*	1900.00*	2316.00*	3168.00*	3267.00*	2039.00*	2455.00*	2768.00*	2826.00*	1998.00*	2277.00*
13	531.00	475.00	354.00	370.00	428.00	458.00	152.00*	152.00*	358.00	239.00	396.00	457.00
14	504.00	622.00	483.00	621.00	498.00	605.00	515.00	596.00	522.00	629.00	516.00	655.00
15	457.00	572.00	513.00	634.00	529.00	641.00	515.00*	653.00*	514.00*	565.00*	546.00*	664.00*
16	430.00	408.00	267.00*	413.00*	291.00	517.00	440.00	692.00	370.00	602.00	317.00	587.00
17	746.00*	588.00	581.00*	542.00*	383.00	415.00	318.00	372.00	268.00	277.00	317.00	352.00
18	499.00	720.00	416.00	479.00	342.00	481.00	453.00	497.00	532.00	693.00	397.00	452.00
19	388.00	426.00	341.00	378.00	431.00	477.00	340.00	410.00	215.00	371.00	411.00	422.00
20	418.00	447.00	386.00	415.00	299.00	406.00	402.00	447.00	397.00	407.00	364.00	448.00

TABLE 34. RAW DATA FOR 1,2-DICHLOROBENZENE ANALYSIS BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	2	1	2	1	2	1	2	1	2	1	2
TRUE CONC:	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
LAB NUMBER												
1	1.93	2.62	1.97	2.42	1.97	2.41	1.38	1.48	1.25*	1.02*	1.19	0.57
2	1.80	3.10	2.08	3.11	2.65	3.61	0.00*	3.96	3.04	4.23	2.04	2.89
3	2.60	3.37	2.17	3.32	1.76*	1.58*	1.77	2.24	1.27	2.53	1.41	1.64
4	2.16	2.89	2.06	2.84	2.12	2.91	1.78	2.35	2.07	2.55	1.81	2.77
5	1.53	1.83	2.42	2.33	2.19	3.02	1.04	3.11	1.82	2.01	2.34	3.12
6	2.82	2.59	1.88	2.59	2.18	2.59	2.47	3.18	4.12	2.94	4.59*	1.30
7	2.31	2.93	3.85	2.82	1.83	2.95	2.32	3.07	2.00	2.51	1.51	2.64
8	1.29	1.99	1.54	1.80	1.77	2.50	1.83	2.27	1.92	2.77	1.66	2.05
9	4.72	6.37*	3.99	1.51	5.65*	9.71*	10.60*	7.53	0.00*	0.00*	0.31	0.00*
10	2.36	2.76	2.58	3.50	2.35	2.07	2.74	8.30	6.26	5.93	7.90*	10.90*
11	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.05	0.00*	0.00*	0.81
12	12.30*	12.30*	5.48*	5.48*	4.11*	4.11*	2.74*	5.48*	4.11*	5.33*	4.11*	5.48*
13	1.47	1.91	1.39	2.65	1.33	1.80	2.32	2.53	17.60*	18.60*	0.32	1.82
14	2.28	2.80	2.06	3.32	2.33	3.05	2.17	3.87	3.35	4.93	2.06	2.78
15	3.88	4.54	4.03	3.55	3.70*	4.48*	5.60*	4.61*	6.84	3.64	3.59*	4.40*
16	6.12	4.68	0.78*	0.31*	2.18	2.13	3.67	3.23	2.63	2.78	2.65	3.41
17	11.50*	9.70*	3.88	3.57	6.56*	4.96	1.38	5.60	13.10*	0.00*	1.63	1.99
18	5.11	0.00*	2.69	3.36	3.53*	5.29	0.00*	0.00*	2.44	3.66	0.00*	0.23
19	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*	1.98	0.00*	0.00*	0.00*	0.00*
20	2.21	2.81	2.92	3.41	2.17	2.61	2.03	2.61	1.17	5.65	2.20	3.63

TABLE 34 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
LAB NUMBER												
1	43.00	43.80	36.30	45.10	35.60	41.50	36.60	32.60	36.20*	32.90*	32.70	38.60
2	45.60	48.50	41.10	49.60	40.00	42.40	41.10	49.30	41.60	42.80	38.40	42.00
3	59.30	58.00	54.60	59.50	37.20*	35.80*	39.20	41.00	41.30	40.40	38.50	43.30
4	41.10	45.60	42.80	46.30	43.30	47.40	44.40	46.60	40.90	46.30	42.80	45.50
5	43.70	43.60	40.70	45.00	41.20	46.80	51.70	50.90	42.70	44.50	41.90	43.20
6	43.20	58.00	42.40	49.60	43.20	51.20	44.80	60.00	42.90	62.00	42.90	57.30
7	39.70	46.30	40.30	42.10	42.00	45.20	42.50	46.80	42.00	46.00	43.10	48.20
8	40.80	35.40	46.20	37.10	47.00	37.70	46.60	39.90	51.20	39.60	37.40	38.40
9	53.80	67.00	56.00	61.40	56.20	58.60	45.70	57.30	51.90	55.60	49.60	56.00
10	55.10	55.50	53.00	56.50	63.90	53.80	53.40	48.60	60.50	52.80	47.80*	65.30*
11	45.70	49.40	41.80	53.10	47.90	56.10	41.30	58.30	44.80	53.60	44.90	74.20
12	170.00*	170.00*	192.00*	181.00*	254.00*	145.00*	214.00*	237.00*	282.00*	135.00*	192.00*	136.00*
13	66.50	65.60	45.40	47.60	56.90	56.90	55.50	60.30	63.40	68.40	45.70	47.90
14	47.80	52.50	49.00	52.90	48.60	52.90	52.20	55.30	52.10	55.40	50.80	55.10
15	46.60	62.70	53.50	59.30	57.20*	60.70*	55.80*	60.20*	57.10	60.50	69.40*	62.50*
16	22.00	35.40	28.10*	16.80*	39.50	25.40*	26.00	43.40	38.20	28.10	34.10	55.90
17	72.10	28.90	105.00*	67.50	46.60	45.80	51.10	54.10	56.40	43.60	45.90	22.40
18	59.30	55.00	46.70	45.50	46.90	55.20	105.00*	137.00*	52.00	62.00	46.70	59.60
19	39.70*	41.80*	36.80	57.30	37.80	48.50	33.60	35.30	36.00*	40.40*	30.80*	33.50*
20	41.10	42.50	45.40	48.90	43.70	46.90	39.10	44.10	44.40	47.00	43.90	43.90

TABLE 34 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	5	6	5	6	5	6	5	6	5	6	5	6
TRUE CONC:	449.00	600.00	449.00	600.00	449.00	600.00	449.00	600.00	449.00	600.00	449.00	600.00
LAB NUMBER												
1	301.00	359.00	267.00	344.00	263.00	313.00	257.00	476.00	295.00*	374.00*	377.00	315.00
2	427.00	468.00	419.00	487.00	398.00	504.00	421.00	472.00	430.00	536.00	407.00	502.00
3	492.00	476.00	426.00	490.00	342.00*	437.00*	361.00	430.00	363.00	461.00	345.00	440.00
4	431.00	530.00	436.00	526.00	447.00	540.00	408.00	516.00	428.00	519.00	416.00	508.00
5	449.00	559.00	431.00	491.00	431.00	548.00	459.00	505.00	448.00	553.00	442.00	549.00
6	436.00	400.00	452.00	395.00	400.00	384.00	472.00	405.00	440.00	411.00	421.00	408.00
7	430.00	559.00	408.00	531.00	392.00	507.00	306.00	522.00	407.00	491.00	429.00	534.00
8	550.00	518.00	573.00	547.00	564.00	543.00	571.00	535.00	519.00	555.00	577.00	497.00
9	328.00	376.00	324.00	380.00	394.00	357.00	402.00	382.00	401.00	513.00	452.00	364.00
10	610.00	700.00	592.00	729.00	507.00	826.00*	715.00	796.00	631.00	694.00	485.00*	638.00*
11	511.00	587.00	387.00	607.00	444.00	598.00	488.00	592.00	524.00	633.00	591.00	601.00
12	1356.00*	1356.00*	1356.00*	1695.00*	1582.00*	1921.00*	1582.00*	1808.00*	1469.00*	1695.00*	1469.00*	1921.00*
13	542.00	473.00	352.00	361.00	376.00	432.00	137.00	128.00	521.00	427.00	433.00	472.00
14	427.00	546.00	406.00	513.00	434.00	515.00	473.00	530.00	444.00	566.00	453.00	568.00
15	512.00	652.00	553.00	693.00	574.00*	698.00*	534.00*	689.00*	572.00	697.00	585.00*	715.00*
16	408.00	338.00	234.00*	337.00*	225.00	444.00	440.00	581.00	328.00	534.00	271.00	431.00
17	432.00	313.00	564.00	453.00	392.00	476.00	324.00	414.00	254.00	421.00	376.00	416.00
18	435.00	775.00	403.00	501.00	353.00	491.00	427.00	531.00	509.00	634.00	414.00	508.00
19	384.00*	410.00*	361.00	398.00	450.00	515.00	368.00	408.00	296.00*	410.00*	354.00*	434.00*
20	328.00	374.00	333.00	340.00	232.00	295.00	338.00	372.00	345.00	343.00	327.00	361.00

TABLE 35. RAW DATA FOR 1,3-DICHLOROBENZENE ANALYSIS BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	2	1	2	1	2	1	2	1	2	1	2
TRUE CONC:	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
LAB NUMBER												
1	2.08	2.73	2.15	2.55	2.18	2.43	1.44	0.00*	1.47*	1.41*	1.34*	1.26*
2	1.76	3.29	1.92	2.70	3.02	3.95	0.00*	9.50	5.13	7.46*	2.08	3.31
3	2.40	3.22	2.22	3.23	1.65*	1.87*	0.00*	0.00*	1.65	2.30	2.04	2.07
4	2.38	3.10	2.26	3.05	2.34	3.11	0.00*	0.00*	2.24	2.81	2.21	3.17
5	1.51	1.80	2.34	2.82	1.97	2.85	0.00*	0.00*	1.14	1.80	1.69	3.31
6	1.66	2.28	1.59	2.48	1.66	2.28	0.00*	0.00*	0.00*	0.00*	0.96	1.17
7	2.08	3.09	4.46	2.88	2.20	2.87	3.78	4.80	3.55	2.44	1.67	3.80
8	1.44	1.88	1.64	2.25	1.24	2.45	0.00*	18.00	3.38	3.38	1.24	1.76
9	9.53*	10.70*	11.40*	5.35*	6.19	9.61*	0.00*	0.00*	0.00*	0.25	1.44	0.00*
10	2.26	2.60	2.09	3.10	2.53	2.82	1.93	6.90	2.62	0.00*	3.24	2.34
11	0.00*	0.03*	0.00*	0.00*	0.28	0.33	1.85	2.14	2.44	0.00*	0.00*	4.07
12	5.41*	6.76*	4.06*	4.06*	3.38*	4.06*	0.00*	0.00*	2.70*	4.43*	0.00*	6.76*
13	1.74	2.28	1.38	1.74	1.39	1.77	0.00*	20.80	23.10*	25.90*	2.71	4.00
14	2.63	3.47	2.59	3.96	2.97	3.61	3.90	3.80	3.40	4.32	2.70	4.08
15	2.87	3.46	3.65	2.68	3.14	3.56	6.50	8.70	8.65*	3.73	3.65*	4.27*
16	2.63	4.18	1.60*	1.35*	3.62	3.29	11.50*	18.90	2.62	1.45	3.99	3.72
17	11.00*	6.70*	9.14*	9.94*	5.86	5.57	*	*	13.90*	*	2.67	2.57
18	4.98*	2.28	2.28	2.90	2.61	3.05	4.40	0.00*	5.88	10.10*	2.29	3.05
19	1.47	2.04	1.60	2.39	1.60	2.59	0.00*	0.00*	1.58	2.36	0.00*	0.00*
20	2.20	2.83	3.18	3.51	1.97	2.65	0.00*	0.00*	1.42	3.93	1.74	2.90

TABLE 35 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
LAB NUMBER												
1	42.60	47.00	34.90	48.80	35.10	44.20	132.50*	107.00	37.50*	36.10*	34.80*	43.60*
2	46.10	52.40	41.50	53.80	42.10	48.80	42.30	56.50	45.30	43.30	43.50	48.00
3	60.00	62.10	57.00	64.20	34.70*	38.50*	31.70	32.40	37.90	42.20	37.10	48.90
4	46.40	56.00	48.50	56.70	47.50	57.00	44.00	48.60	44.30	54.30	47.80	54.40
5	42.60	46.10	37.90	46.10	40.30	47.50	41.50	45.10	42.50	49.40	42.00	47.80
6	44.10	50.00	42.30	48.80	41.20	52.90	42.50	57.60	42.50	90.00*	42.50	48.70
7	41.30	52.20	41.20	47.60	43.80	49.80	67.50	53.80	42.30	50.00	46.80	55.30
8	43.40	40.50	47.70	46.60	42.40	41.80	68.00	53.00	42.90	46.10	49.30	49.70
9	54.70	68.30	59.10	68.10	59.30	67.00	21.70	42.00	45.80	53.20	43.20	46.90
10	47.80	47.80	46.80	52.30	40.90	46.70	46.70	62.10	43.80	49.00	47.30	43.30
11	44.90	50.00	46.90	54.00	49.10	52.20	64.90	76.30	49.30	54.00	42.80	66.40
12	187.00*	201.00*	169.00*	222.00*	180.00*	318.00*	291.00*	347.00*	312.00*	173.00*	208.00*	166.00*
13	68.30	68.30	45.40	50.20	63.50	62.60	37.00	33.40	28.00	32.30	43.40	49.40
14	52.30	61.50	53.60	62.00	53.60	62.00	58.40	66.40	56.20	65.80	55.30	65.00
15	40.70	60.70	48.10	57.30	50.90	58.00	48.60	55.60	52.50	58.00	64.80*	62.20*
16	23.30	39.40	29.00*	19.50*	43.70	31.40	51.00	94.00	38.10	31.80	38.70	71.80
17	74.70	30.80	106.00*	75.40*	49.20	51.60	8.90	19.50	42.70	40.00	41.40	48.50
18	48.50	54.20	43.80	50.50	43.40	61.70	244.00*	267.00*	52.30	65.10	51.80	69.60
19	43.10	49.80	40.80	69.30	41.00	58.60	27.90	32.20	40.00	50.50	32.80	39.00
20	40.50	45.90	46.10	50.60	43.70	50.20	25.80	34.30	43.10	50.30	41.20	45.10

TABLE 35 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	5	6	5	6	5	6	5	6	5	6	5	6
TRUE CONC:	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
LAB NUMBER												
1	33.60*	411.00	279.00	370.00	285.00	339.00	1670.00*	1650.00*	302.00*	369.00*	402.00*	328.00*
2	441.00	492.00	456.00	520.00	452.00	528.00	413.00	481.00	427.00	549.00	408.00	525.00
3	501.00	480.00	435.00	503.00	357.00*	442.00*	368.00	429.00	379.00	471.00	367.00	473.00
4	460.00	565.00	458.00	564.00	473.00	582.00	413.00	560.00	477.00	583.00	467.00	567.00
5	434.00	530.00	393.00	452.00	415.00	501.00	418.00	465.00	427.00	521.00	403.00	509.00
6	416.00	396.00	429.00	392.00	408.00	392.00	444.00	407.00	417.00	384.00	407.00	408.00
7	443.00	577.00	423.00	547.00	430.00	532.00	419.00	601.00	415.00	508.00	448.00	549.00
8	613.00	558.00	645.00*	574.00	642.00	581.00	645.00	532.00	599.00	529.00	602.00	582.00
9	307.00	343.00	298.00	346.00	377.00	336.00	280.00	293.00	357.00	498.00	453.00	366.00
10	392.00	426.00	375.00	487.00	353.00	463.00	353.00	425.00	419.00	413.00	310.00	398.00
11	444.00	572.00	446.00	588.00	480.00	581.00	534.00	602.00	540.00	606.00	580.00	542.00
12	1805.00*	1736.00*	1666.00*	2291.00*	2013.00*	2429.00*	2083.00*	2430.00*	1874.00*	2290.00*	1943.00*	2498.00*
13	512.00	466.00	346.00	358.00	397.00	450.00	80.30	80.30*	568.00	430.00	425.00	448.00
14	454.00	582.00	434.00	553.00	461.00	549.00	495.00	565.00	508.00	634.00	477.00	605.00
15	437.00	584.00	497.00	630.00	519.00	636.00	466.00	610.00	522.00	636.00	530.00*	652.00*
16	449.00	404.00	245.00*	418.00*	257.00	504.00	463.00	647.00	366.00	560.00	300.00	502.00
17	450.00	344.00	606.00*	516.00*	414.00	470.00	331.00	407.00	206.00	288.00	361.00	407.00
18	508.00	792.00*	405.00	505.00	343.00	487.00	614.00	723.00	518.00	647.00	411.00	511.00
19	409.00	431.00	398.00	427.00	495.00	560.00	388.00	433.00	330.00	466.00	430.00	460.00
20	320.00	354.00	320.00	326.00	223.00	277.00	325.00	351.00	333.00	322.00	322.00	343.00

TABLE 36. RAW DATA FOR 1,4-DICHLOROBENZENE ANALYSIS BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	2	1	2	1	2	1	2	1	2	1	2
TRUE CONC:	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
LAB NUMBER												
1	2.02	2.76	2.04	2.54	2.03	2.42	1.34	1.43	1.35*	1.44*	1.31*	1.32*
2	1.45	2.86	1.49	2.35	2.51	3.51	3.10	4.94	2.67	3.29	2.14	3.73
3	2.55	3.39	2.23	3.41	1.59	1.95	4.71	2.89	1.88	2.70	1.87	1.72
4	2.26	3.16	2.21	3.12	2.21	3.16	1.28	2.04	2.11	2.81	2.19	2.82
5	1.43	1.69	2.65	2.70	1.61	2.58	2.43	3.72	1.14	1.51	2.14	3.61
6	2.00	2.93	1.87	3.07	2.00	2.93	2.40	3.20	2.86	4.27	2.40	2.00
7	1.98	3.11	4.37	2.81	2.12	2.91	2.13	4.48	3.08	1.99	1.77	3.35
8	1.36	1.98	1.45	1.61	1.19	1.96	0.00*	0.00*	1.42	3.30	1.84	1.50
9	5.79*	7.50*	0.00*	2.83	5.06	5.66	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
10	1.86	2.46	2.29	3.70	1.97	2.78	18.00*	0.00*	6.59*	7.78	4.01*	5.27
11	0.00*	0.00*	0.00*	0.28*	0.35	0.34	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*
12	4.27*	6.10*	4.27*	4.27*	3.05*	3.97*	0.00*	0.00*	3.05*	5.12*	0.00*	5.00
13	1.92	2.54	1.42	1.79	1.37	1.81	1.89	4.20	16.40*	20.90*	1.51	3.00
14	2.16	2.78	1.95	3.35	2.34	3.08	1.84	5.06	2.24	3.58	2.20	2.87
15	3.27	3.89	3.68	2.69	3.19*	3.77*	3.05	2.44	8.09*	3.88	4.14*	4.90*
16	0.11	0.52	0.92*	0.42*	3.66	3.69	0.00*	0.00*	0.00*	3.13	2.66	2.73
17	14.70*	11.00*	7.88*	8.38*	5.29	5.32	7.03*	8.94*	27.80*	7.67	3.11	2.65
18	4.29	1.65	1.99	3.38	1.93	2.63	0.00*	0.00*	1.05	6.57	1.57	2.10
19	1.58	2.19	1.74	2.49	0.84	1.71	0.00*	0.00*	1.40	2.44	1.42	1.26
20	2.35	3.14	3.46	3.57	1.87	2.60	0.00*	2.45	2.29	4.31	1.97	3.23

TABLE 36 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
LAB NUMBER												
1	41.40	45.20	34.70	46.70	34.40	43.20	39.70	40.50	32.50*	31.30*	29.20*	37.70*
2	44.80	50.60	40.40	51.60	41.00	47.00	45.00	52.30	40.40	42.90	40.80	46.80
3	65.00	65.90	61.80*	68.40	36.10	39.90	41.80	46.00	39.70	43.50	37.20	46.30
4	43.10	51.90	45.10	53.00	45.60	53.80	49.70	54.90	42.80	52.00	46.00	52.30
5	45.00	47.50	40.90	49.30	42.00	48.90	49.10	55.70	43.90	50.70	43.60	47.80
6	41.70	50.00	43.50	50.40	43.50	53.00	45.20	48.70	45.20	58.00	46.10	50.00
7	41.30	51.70	41.40	47.20	43.90	49.50	49.80	53.60	41.80	49.20	46.30	54.50
8	41.30	38.60	46.30	36.90	44.60	40.10	37.70	42.70	48.70	41.40	42.40	49.00
9	50.30	59.50	53.60	59.10	53.70	58.20	30.90	45.30	46.60	53.00	47.90	52.90
10	45.00	45.00	46.00	49.30	51.80	55.10	34.00	39.00	55.00	40.30	36.40	44.70
11	42.30	47.20	40.80	51.70	50.20	50.70	35.50	48.70	44.20	47.50	39.40	63.20
12	155.00*	165.00*	201.00*	180.00*	185.00*	270.00*	237.00*	230.00*	240.00*	135.00*	165.00*	135.00*
13	71.10	71.60	47.70	52.20	57.10	43.10	42.50	57.70	73.60*	72.30	43.00	49.80
14	46.80	54.90	49.50	55.50	47.80	55.20	50.80	58.10	51.10	61.10	44.00	58.20
15	42.10	55.50	48.70	58.00	52.10*	59.10*	42.20	49.60	53.10	60.00	64.50*	61.20*
16	19.70	37.80	30.10*	19.20*	44.00	30.50	0.00*	0.00*	41.10	34.40	39.00	63.30
17	77.90	34.40	104.00*	72.80*	49.40	51.60	56.20	61.50	53.60	51.20	44.00	50.20
18	48.80	51.80	43.50	49.80	38.70	54.40	10.50*	28.00	45.90	59.30	46.60	61.40
19	40.10	45.40	38.00	61.90	36.80	51.10	31.20	36.50	36.80	44.20	30.60	35.80
20	44.60	51.20	46.40	53.10	45.20	51.10	41.40	47.10	49.50	57.20	42.40	48.00

TABLE 36 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	5	6	5	6	5	6	5	6	5	6	5	6
TRUE CONC:	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
LAB NUMBER												
1	313.00	378.00	267.00	350.00	269.00	319.00	1240.00*	1230.00*	219.00*	302.00*	315.00*	247.00*
2	432.00	473.00	446.00	515.00	419.00	521.00	391.00	510.00	418.00	537.00	421.00	521.00
3	500.00	492.00	448.00	502.00	376.00	458.00	394.00	448.00	396.00	487.00	375.00	466.00
4	441.00	539.00	439.00	539.00	450.00	555.00	419.00	540.00	447.00	550.00	440.00	533.00
5	454.00	555.00	409.00	471.00	441.00	538.00	437.00	499.00	446.00	530.00	420.00	550.00
6	436.00	400.00	476.00	394.00	440.00	383.00	480.00	411.00	468.00	417.00	456.00	423.00
7	443.00	577.00	422.00	546.00	408.00	529.00	369.00	538.00	414.00	506.00	445.00	549.00
8	489.00	525.00	472.00	537.00	504.00	510.00	511.00	508.00	509.00	540.00	507.00	537.00
9	273.00	304.00	260.00	318.00	263.00	319.00	267.00	308.00	386.00	468.00	334.00	428.00
10	342.00	393.00	328.00	440.00	354.00	294.00	428.00	420.00	312.00	425.00	299.00	395.00
11	445.00	575.00	442.00	592.00	473.00	587.00	507.00	575.00	531.00	609.00	581.00	557.00
12	1350.00*	1350.00*	1250.00*	1700.00*	1550.00*	1850.00*	1500.00*	1800.00*	1450.00*	1750.00*	1500.00*	1900.00*
13	544.00	494.00	361.00	372.00	387.00	431.00	177.00	145.00*	546.00	434.00	422.00	460.00
14	425.00	542.00	405.00	514.00	429.00	512.00	465.00	539.00	443.00	553.00	446.00	564.00
15	457.00	578.00	494.00	621.00	513.00*	626.00*	463.00	602.00	521.00	628.00	526.00*	644.00*
16	448.00	391.00	257.00*	404.00*	252.00	465.00	437.00	627.00	348.00	553.00	278.00	494.00
17	386.00	300.00	495.00*	458.00*	340.00	377.00	317.00	383.00	222.00	301.00	343.00	380.00
18	468.00	741.00	368.00	455.00	320.00	450.00	350.00	438.00	454.00	558.00	377.00	472.00
19	365.00	386.00	349.00	392.00	430.00	493.00	349.00	400.00	291.00	407.00	372.00	408.00
20	351.00	375.00	343.00	345.00	234.00	293.00	346.00	380.00	354.00	351.00	341.00	370.00

TABLE 37. RAW DATA FOR ETHYLBENZENE ANALYSIS BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	2	1	2	1	2	1	2	1	2	1	2
TRUE CONC:	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00	2.20	3.00
LAB NUMBER												
1	2.13	2.70	2.22	2.64	2.24	2.44	3.91	3.50	2.86	1.29	2.19	0.59
2	1.99	3.49	2.03	2.73	3.11	3.83	2.76	4.24	2.32	3.41	0.00*	0.00*
3	2.14	3.69	2.02	2.85	1.63	4.98	2.45	1.78	1.30	1.29	2.61	3.08
4	2.34	2.88	2.24	2.96	2.01	2.75	1.08	1.90	1.83	2.38	3.61	3.70
5	2.03	2.61	1.47	1.87	2.16	2.94	1.97	2.84	2.50	3.75	4.10	2.98
6	2.24	2.94	2.12	3.06	2.24	3.06	2.35	2.28	2.00	1.76	3.06	1.89
7	1.69	3.01	3.54	2.86	2.05	2.94	1.97	3.08	2.26	0.44	0.00*	2.03
8	1.48	1.92	1.76	2.15	1.44	1.76	2.96	2.19	2.55	3.09	5.30	4.40
9	7.29*	8.90*	4.34	5.93	3.91	13.00*	4.25	4.89	0.00*	0.76	0.00*	0.00*
10	1.87	2.84	2.53	3.05	1.92	2.42	3.28	2.34	3.86	4.66	3.10	5.30
11	0.32*	0.51*	0.73	0.85	0.57	0.93	0.81*	1.11*	0.77	0.90	2.41	2.16
12	2.44	2.23	3.60*	3.90*	2.95*	3.84*	5.49*	7.93*	5.31*	2.33*	10.00*	10.60*
13	4.91	19.50*	5.91	5.67	13.30*	14.20*	0.15*	2.44*	9.59*	9.80*	0.00*	0.00*
14	2.72	3.37	2.43	3.87	2.83	3.66	1.98	4.79	3.35	4.29	1.14	2.33
15	3.34	4.09	3.68	3.01	3.21	3.97	3.81	3.12	6.82*	4.56*	3.92*	4.88*
16	3.67	0.87	1.56*	1.88*	1.38*	2.23*	2.40	3.50	1.15	2.02	2.76	1.72
17	3.91	6.71*	19.20*	20.30*	5.63*	7.36*	2.62	4.03	5.58*	4.68	3.20	0.70
18	0.89	4.69	0.00*	0.00*	12.40*	4.54	0.53	0.00*	2.31	3.94	6.10	13.00*
19	2.38	2.79	1.93	2.62	1.68	2.31	1.82	2.08	2.14	2.46	3.37	2.77
20	2.13	2.75	3.58	3.04	2.10	2.96	2.27	2.62	1.43	0.77	1.19	1.87

TABLE 37 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
LAB NUMBER												
1	40.50	44.60	32.80	47.20	34.60	40.30	42.10	39.20	41.60	36.90	36.70	47.50
2	45.60	51.80	41.60	53.70	41.40	49.00	43.40	50.30	37.00	45.50	66.00	44.40
3	26.20	80.40	83.90*	89.60	27.10	29.80	29.00	32.20	28.70	29.80	26.80	32.10
4	41.70	50.90	44.10	52.40	45.30	53.50	42.80	52.30	38.40	52.40	50.10	55.70
5	47.70	51.40	42.90	53.00	40.30	47.20	44.80	54.10	41.10	48.50	42.80	47.80
6	41.50	50.90	43.00	51.10	42.20	52.60	40.70	63.60	43.00	58.20	42.20	53.60
7	42.00	52.00	41.30	47.40	43.50	50.60	47.70	56.50	36.90	43.00	43.60	54.30
8	47.80	45.20	45.80	41.40	44.30	43.40	50.60	41.00	53.30	48.60	56.40	39.70
9	56.40	68.10	61.30	69.60	61.10	66.00	43.90	60.00	44.80	52.10	43.20	48.50
10	47.60	55.30	45.60	53.20	60.00	54.20	44.50	65.50	53.60	56.90	47.00	52.70
11	37.10*	32.70*	44.50	33.60	42.50	34.20	30.30*	33.00*	37.60	32.10	31.90	36.50
12	120.00*	133.00*	165.00*	198.00*	244.00*	213.00*	280.00*	209.00*	271.00*	263.00*	189.00*	197.00*
13	84.10	92.90	61.00	68.70	97.40*	102.00*	32.80*	36.50*	3.40*	4.50	39.50	51.00
14	54.80	64.60	56.10	65.10	55.40	65.00	57.80	87.80	55.90	66.20	58.00	69.00
15	43.40	61.50	51.00	60.50	54.60	60.80	52.80	60.70	53.80*	60.00*	67.00*	62.10*
16	24.30	35.70	29.10*	22.20*	33.10*	28.60*	25.50	36.30	30.00	28.70	28.60	62.40
17	80.70	31.00	108.00*	81.50	55.20	58.50	54.50	55.60	48.80	49.20	35.70	41.70
18	25.40	28.40	64.80	63.70	59.30	66.20	66.10	67.60	54.80	77.10	64.20	75.50
19	41.90	44.40	37.10	63.00	37.40	52.00	34.50	41.60	37.60	44.40	32.60	38.40
20	44.10	52.00	42.10	52.90	43.70	47.10	47.00	53.50	48.80	56.20	42.50	45.60

TABLE 37 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	5	6	5	6	5	6	5	6	5	6	5	6
TRUE CONC:	452.00	551.00	452.00	551.00	452.00	551.00	452.00	551.00	452.00	551.00	452.00	551.00
LAB NUMBER												
1	344.00	451.00	259.00	369.00	282.00	353.00	319.00	330.00	341.00	390.00	328.00	316.00
2	384.00	422.00	408.00	484.00	372.00	488.00	316.00	502.00	360.00	495.00	365.00	471.00
3	531.00	549.00	504.00	563.00	465.00	568.00	481.00	541.00	467.00	567.00	449.00	535.00
4	416.00	527.00	416.00	529.00	425.00	545.00	386.00	527.00	435.00	545.00	427.00	530.00
5	434.00	539.00	401.00	488.00	426.00	532.00	405.00	501.00	451.00	541.00	409.00	521.00
6	444.00	400.00	480.00	400.00	444.00	390.00	487.00	410.00	469.00	410.00	455.00	421.00
7	423.00	556.00	406.00	545.00	393.00	524.00	356.00	535.00	379.00	480.00	424.00	545.00
8	562.00	594.00	602.00	613.00	572.00	638.00	545.00	559.00	573.00	569.00	566.00	587.00
9	281.00	326.00	259.00	328.00	249.00	303.00	292.00	339.00	342.00	421.00	527.00	541.00
10	448.00	531.00	462.00	603.00	414.00	473.00	417.00	469.00	455.00	513.00	363.00	529.00
11	295.00*	384.00*	311.00	396.00	309.00	400.00	318.00*	405.00*	310.00	388.00	310.00	387.00
12	1405.00*	1346.00*	2036.00*	2626.00*	2507.00*	2566.00*	2088.00*	2697.00*	2154.00*	2124.00*	2153.00*	2507.00*
13	515.00	445.00	455.00	423.00	538.00*	621.00*	68.50*	82.00*	304.00	234.00	478.00	568.00
14	488.00	628.00	465.00	620.00	477.00	606.00	525.00	622.00	506.00	647.00	500.00	662.00
15	461.00	593.00	506.00	658.00	525.00	666.00	495.00	664.00	523.00*	657.00*	539.00*	691.00*
16	333.00	341.00	228.00*	357.00*	262.00*	427.00*	387.00	581.00	339.00	505.00	314.00	542.00
17	259.00	309.00	478.00	468.00	341.00	384.00	336.00	370.00	222.00	267.00	328.00	368.00
18	567.00	881.00*	455.00	543.00	389.00	538.00	463.00	623.00	424.00	509.00	410.00	505.00
19	339.00	381.00	346.00	390.00	421.00	482.00	320.00	368.00	285.00	407.00	428.00	458.00
20	356.00	412.00	346.00	370.00	254.00	341.00	370.00	424.00	363.00	389.00	350.00	400.00

TABLE 38. RAW DATA FOR TOLUENE ANALYSIS BY WATER TYPE

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	1	2	1	2	1	2	1	2	1	2	1	2
TRUE CONC:	2.10	3.00	2.10	3.00	2.10	3.00	2.10	3.00	2.10	3.00	2.10	3.00
LAB NUMBER												
1	2.15	2.73	2.22	2.64	2.22	2.44	3.16	2.22	5.45	4.26	1.21	0.60
2	2.38	3.88	2.29	2.99	1.50	2.06	1.96	4.01	0.00*	11.00	5.08	8.59
3	1.70	3.80	1.95	2.34	1.22	1.33	2.29	0.21	0.00*	0.00*	0.46	0.82
4	2.52	3.28	2.55	3.43	2.41	3.31	2.52	3.57	0.00*	0.00*	3.61	3.19
5	2.69	3.52	1.65	2.63	1.68	2.21	2.97	2.54	0.00*	0.00*	0.00*	0.00*
6	2.18	1.76	2.12	2.94	2.24	3.06	2.24	1.53	2.00	1.76	2.59	1.65
7	1.75	3.15	2.97	3.02	2.09	2.94	7.62*	7.60	20.00	0.00*	0.00*	0.00*
8	1.50	3.65	1.53	3.88	1.73	3.21	2.18	5.14	0.00*	12.00	5.80	6.00
9	6.64	6.91*	5.10*	4.23	7.11*	7.46	4.65	1.63	0.00*	0.00*	0.00*	0.00*
10	1.48*	2.00*	1.64	2.25	1.53	1.75	2.31	3.00	0.00*	3.00	1.70	1.80
11	1.37	2.91	1.27	2.06	1.58	1.78	0.00*	4.89	30.60	15.60	6.60	0.00*
12	2.64	1.92	2.76*	3.12*	2.16*	3.12*	0.00*	0.00*	13.80	0.00*	0.00*	0.00*
13	2.11	3.79	1.52	1.68	7.05*	6.91	1.24	4.06	0.00*	0.00*	3.30	5.06
14	2.47	3.06	2.20	3.59	2.60	3.46	0.00*	3.00	0.00*	1.00	2.40	8.80
15	2.98	3.86	3.61	3.28	2.97	4.03	3.26	3.85	69.00*	69.00*	3.64	5.07
16	5.04	3.13	0.87*	1.03*	1.51	0.94	3.97	10.70*	0.00*	3.00	3.33	1.43
17	7.18	15.80*	13.50*	12.80*	8.65*	8.96*	0.00*	7.00	*	*	*	*
18	1.42	1.93	2.14	3.00	2.12	1.74	5.29	2.27	0.00*	0.00*	2.10	21.90*
19	2.62	9.82*	3.18	3.61	1.21	1.35	20.80*	24.20*	3.00	2.00	2.20	2.30
20	2.05	2.89	1.48	2.68	1.90	2.85	1.98	2.61	0.00*	0.00*	0.90	1.00

TABLE 38 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	3	4	3	4	3	4	3	4	3	4	3	4
TRUE CONC:	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00	46.00	54.00
LAB NUMBER												
1	39.40	43.80	32.30	45.90	33.50	39.70	49.10	44.70	106.00	46.00	45.60	57.20
2	41.40	46.70	38.10	50.10	36.20	42.50	36.00	42.70	25.00	38.00	37.10	45.90
3	102.00*	91.80*	99.90*	71.70	21.10	23.20	21.90	24.30	83.70	72.00*	19.40	23.70
4	48.00	59.40	51.20	61.10	51.90	62.30	50.10	62.00	35.60	43.80	51.90	57.00
5	45.60	50.70	45.00	53.70	40.90	48.40	47.10	53.60	26.70	31.80	40.00	42.20
6	40.80	46.40	41.50	45.40	40.00	46.10	40.00	50.90	40.80	53.60	40.80	50.90
7	40.60	51.20	40.40	46.40	44.20	51.30	50.70	58.50	34.00	38.00	37.40	47.60
8	42.70	42.70	44.90	39.60	46.20	46.90	46.30	43.00	56.00	44.00	53.20	48.90
9	51.40	63.30	57.00	69.90	54.80	59.90	35.20	36.00	66.60	87.30*	61.40	54.10
10	33.40*	43.40*	35.00	45.20	37.60	48.60	30.30	50.60	59.00	33.00	30.20	50.40
11	42.90	36.60	51.20	36.60	42.60	38.30	39.50	41.50	65.60	54.60	31.40	34.20
12	149.00*	180.00*	154.00*	178.00*	155.00*	205.00*	152.00*	198.00*	70.80	39.80	100.00*	196.00*
13	55.80	65.40	41.20	49.00	65.70	70.30	31.60	32.00	69.20	36.50	32.80	45.70
14	50.10	59.20	51.90	60.40	50.90	59.90	42.90	52.70	53.00	50.00	54.10	65.10
15	42.50	61.40	48.20	54.60	51.90	59.90	46.60	51.90	149.00*	148.00*	56.90	51.90
16	29.50	44.10	31.10*	23.30*	36.40	33.70	39.50	52.20	21.00	0.00*	36.90	63.10
17	81.00*	34.30	106.00*	77.30*	60.70*	64.30*	34.80	21.60	*	*	21.50*	25.00*
18	55.60	62.80	64.70	64.70	53.90	56.90	48.90	59.10	0.00*	0.00*	56.40	60.60
19	40.90	44.60	36.60	61.30	35.30	53.40	45.20	41.90	41.00	45.00	41.30	38.50
20	41.80	49.60	38.00	49.50	44.60	49.60	45.50	63.10	39.00	44.00	41.10	36.30

TABLE 38 (continued)

	DISTILLED WATER		TAP WATER		SURFACE WATER		WASTE WATER 1		WASTE WATER 2		WASTE WATER 3	
AMPUL NO:	5	6	5	6	5	6	5	6	5	6	5	6
TRUE CONC:	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00	450.00	550.00
LAB NUMBER												
1	375.00	452.00	278.00	390.00	311.00	383.00	488.00	497.00	809.00*	812.00	333.00	398.00
2	416.00	444.00	441.00	497.00	396.00	499.00	311.00	484.00	327.00	449.00	407.00	489.00
3	547.00	596.00	581.00	638.00	548.00	677.00	542.00	572.00	351.00	445.00	505.00	630.00
4	499.00	609.00	500.00	609.00	508.00	620.00	471.00	615.00	527.00	620.00	512.00	610.00
5	439.00	514.00	408.00	481.00	422.00	534.00	420.00	483.00	390.00	539.00	428.00	529.00
6	404.00	400.00	440.00	389.00	407.00	389.00	440.00	400.00	429.00	*	425.00	411.00
7	431.00	536.00	415.00	536.00	422.00	518.00	364.00	532.00	391.00	476.00	425.00	526.00
8	637.00	561.00	616.00	580.00	641.00	589.00	620.00	533.00	657.00	584.00	601.00	542.00
9	287.00	326.00	269.00	330.00	268.00	325.00	285.00	326.00	318.00	448.00	421.00	430.00
10	336.00*	380.00*	315.00	405.00	331.00	359.00	315.00	299.00	324.00	372.00	267.00	314.00
11	355.00	410.00	352.00	440.00	361.00	445.00	377.00	452.00	385.00	450.00	355.00	424.00
12	1728.00*	1680.00*	1800.00*	2256.00*	2544.00*	2472.00*	1782.00*	2022.00*	2237.00*	2141.00*	1852.00*	1924.00*
13	469.00	427.00	317.00	351.00	421.00	433.00	136.00	133.00	311.00	220.00	365.00	422.00
14	501.00	607.00	482.00	606.00	486.00	593.00	495.00	575.00	531.00	769.00	509.00	648.00
15	485.00	596.00	545.00	682.00	563.00	688.00	514.00	657.00	646.00*	747.00*	569.00	712.00
16	440.00	430.00	273.00*	434.00*	317.00	520.00	458.00	593.00	355.00	553.00	339.00	521.00
17	855.00*	713.00	1156.00*	768.00*	1399.00*	1609.00*	328.00	375.00	275.00	320.00	309.00*	358.00*
18	502.00	755.00	410.00	467.00	378.00	460.00	416.00	541.00	519.00	596.00	388.00	468.00
19	380.00	427.00	343.00	386.00	428.00	468.00	337.00	391.00	255.00	382.00	423.00	464.00
20	391.00	467.00	382.00	429.00	317.00	424.00	428.00	489.00	435.00	459.00	382.00	478.00

TABLE 39. BLANK VALUES IN DISTILLED WATER
(μg/L)

Lab number	Analyte[a]						
	B	CB	1,2-DCB	1,3-DCB	1,4-DCB	EB	T
1	ND[b]	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	ND
3	0.34	0.06	<0.03[c]	<0.03	<0.03	0.04	0.16
4	0.57	0.17	0	0	0	0.18	0.31
5	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0
7	ND	ND	ND	ND	ND	ND	ND
8	0	0	0	0	0	0	0
9	0	0.34	1.21	0.44	1.86	0.37	0.86
10	0	0	0	0	0	0	0
11	0	1.62	3.50	2.76	2.37	1.11	0
12	ND	ND	ND	ND	ND	ND	ND
13	13.9	0	0	0	0	12.9	0
14	ND	ND	ND	ND	ND	ND	ND
15	0	0.75	0	0.35	0.36	0.30	0.60
16	0	0.69	0	0	4.42	4.71	0.17
17	0.21	8.89	0.01	4.10	0.70	6.49	4.42
18	0	0.81	0	0	0	2.23	0
19	0	0	0	0	0	0	0
20	0.84	<0.20	<0.40	<0.40	<0.30	<0.20	0.72

[a] Analytes: B = benzene; CB = chlorobenzene;
1,2-DCB = 1,2-dichlorobenzene;
1,3-DCB = 1,3-dichlorobenzene;
1,4-DCB = 1,4-dichlorobenzene;
EB = ethylbenzene; and T = toluene.

[b] ND = not detected.

[c] < = less than.

TABLE 40. BLANK VALUES IN TAP WATER
(µg/L)

Lab number	Analyte[a]						
	B	CB	1,2-DCB	1,3-DCB	1,4-DCB	EB	T
1	ND[b]	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	ND
3	0.46	0.06	<0.03[c]	<0.03	<0.03	<0.03	0.13
4	0.49	0.21	0	0	0	0.14	0.25
5	0	0	0.84	0.64	0.76	0	0
6	0	0	0	0	0	0	0
7	ND	ND	ND	ND	ND	ND	ND
8	0	0	0	0	0	0	0
9	0.34	1.16	3.00	2.73	4.01	0.75	0.76
10	0	0	0	0	0	0	0
11	0	1.12	2.51	1.89	1.56	0.54	0
12	ND	ND	ND	ND	ND	ND	ND
13	2.17	0	0	0	0	6.07	0
14	ND	ND	ND	ND	ND	ND	ND
15	0	0.52	0.05	0	0.07	0.27	0.40
16	0	1.69	0.95	0	0.98	0.66	0
17	0.37	2.98	3.00	2.46	4.32	1.13	<0.01
18	0	0	0	0	0	5.40	0
19	0	0	0	0	0	0	0
20	<0.20	<0.20	0.53	<0.40	<0.30	<0.20	0.58

[a] Analytes: B = benzene; CB = chlorobenzene;
1,2-DCB = 1,2-dichlorobenzene;
1,3-DCB = 1,3-dichlorobenzene;
1,4-DCB = 1,4-dichlorobenzene;
EB = ethylbenzene; and T = toluene.

[b] ND = not detected.

[c] < = less than.

TABLE 41. BLANK VALUES IN SURFACE WATER
(μg/L)

Lab number	Analyte[a]					
	B	CB	1,2-DCB	1,3-DCB	1,4-DCB	EB	T
1	ND[b]	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	1.82
3	<0.3[c]	0.02	0.06	0.18	0.19	0.09	1.46
4	0.23	0.11	0	0	0	0.18	0.44
5	0	0.12	0.03	0.04	0.41	0	0.33
6	0	0	0	0	0	0	0
7	ND	ND	ND	ND	ND	ND	ND
8	0	0	0	0	0	0	0
9	0.19	0	0.30	0	2.60	0.35	0.92
10	0	0	0	0	0	0	0
11	0	1.24	2.93	2.11	1.89	0.78	0
12	ND	ND	ND	ND	ND	ND	ND
13	0	0	0	0	0	2.73	0
14	ND	ND	ND	ND	ND	ND	ND
15	1.65	1.24	0.08	0.18	0.15	0.36	0.70
16	0	0	1.18	0.30	0.68	1.11	0
17	<0.10	2.20	0.98	3.21	3.91	1.17	0.85
18	0.74	1.01	0	0	0.52	0	0
19	0.13	0.37	0	0	1.01	0.30	1.67
20	0.57	<0.20	<0.40	<0.40	0.31	<0.20	0.30

[a] Analytes: B = benzene; CB = chlorobenzene;
1,2-DCB = 1,2-dichlorobenzene;
1,3-DCB = 1,3-dichlorobenzene;
1,4-DCB = 1,4-dichlorobenzene;
EB = ethylbenzene; and T = toluene.

[b] ND = not detected.

[c] < = less than.

TABLE 42. BLANK VALUES IN WASTEWATER 1
(µg/L)

Lab number	Analyte[a]						
	B	CB	1,2-DCB	1,3-DCB	1,4-DCB	EB	T
1	1.05	28.3	0.67	3.45	37.5	1.27	2.12
2	2.52	27.8	5.75	46.5	0.54	0.46	6.59
3	1.81	20.6	<0.03[c]	44.7	0.05	1.19	5.05
4	0.92	41.0	0	72.5	0	1.53	2.34
5	1.91	31.4	0	46.8	0.80	0.36	3.19
6	0	0	0	25.1	0	0	0
7	ND[b]	30.9	ND	ND	ND	0.45	ND
8	1.54	53.7	0	162	0	0.50	2.49
9	4.77	34.9	0	43.6	0	0.92	8.48
10	1.88	72.4	0	0	103	1.25	5.20
11	1.49	18.9	2.32	7.52	1.94	0.38	0
12	ND	20.3	ND	ND	ND	ND	18.0
13	2.19	23.9	0	50.2	0	6.89	3.17
14	3.01	35.2	ND	53.6	ND	0.65	10.4
15	2.46	28.8	0	53.4	0	1.07	0
16	0.43	21.3	0.30	43.6	0	1.77	0
17	1.76	2.53	3.40	90.5	<0.01	2.39	55.4
18	1.10	24.1	4.42	7.20	62.0	2.80	0.86
19	1.83	29.9	0	54.3	0	0.15	8.77
20	2.04	32.4	<0.40	50.4	<0.30	0.36	0.94

[a] Analytes: B = benzene; CB = chlorobenzene;
1,2-DCB = 1,2-dichlorobenzene;
1,3-DCB = 1,3-dichlorobenzene;
1,4-DCB = 1,4-dichlorobenzene;
EB = ethylbenzene; and T = toluene.

[b] ND = not detected.

[c] < = less than.

TABLE 43. BLANK VALUES IN WASTEWATER 2
(μg/L)

Lab number	Analyte[a] B	CB	1,2-DCB	1,3-DCB	1,4-DCB	EB	T
1	2.95	186	0.49	0.13	ND	1.68	85.0
2	5.02	215	ND[b]	ND	ND	2.72	145
3	353	255	<0.03[c]	0.36	<0.03	2.78	221
4	3.76	229	0.61	0.48	0	2.66	143
5	4.30	217	0.52	0.72	0.79	3.42	131
6	0	114	0	170	0	0	0
7	4.61	238	ND	ND	ND	2.95	135
8	5.71	467	0	7.82	0	4.24	192
9	12.6	168	3.14	1.45	3.55	3.67	77.5
10	7.58	421	1.54	0	0	6.64	161
11	3.54	175	2.24	4.11	2.12	0.98	86.4
12	ND	144	ND	ND	ND	ND	91.2
13	42.2	276	0	0	0	12.0	165
14	7.15	278	ND	ND	ND	3.37	150
15	2.92	236	1.98	0.49	0.12	2.78	116
16	2.57	201	1.33	2.60	0	4.25	138
17	10.3	111	1.99	11.2	<0.01	7.22	132
18	2.52	175	0	0	1.31	4.62	132
19	5.73	188	0	0	0	1.97	110
20	4.33	234	1.00	0.47	<0.30	2.95	136

[a] Analytes: B = benzene; CB = chlorobenzene;
1,2-DCB = 1,2-dichlorobenzene;
1,3-DCB = 1,3-dichlorobenzene;
1,4-DCB = 1,4-dichlorobenzene;
EB = ethylbenzene; and T = toluene.

[b] ND = not detected.

[c] < = less than.

TABLE 44. BLANK VALUES IN WASTEWATER 3
(μg/L)

Lab number	Analyte[a]						
	B	CB	1,2-DCB	1,3-DCB	1,4-DCB	EB	T
1	0.47	2.81	0.43	0.23	ND[b]	5.73	7.62
2	0.07	3.84	ND	0.05	0.24	11.1	6.11
3	0.48	2.02	<0.03[c]	<0.03	<0.03	4.89	5.66
4	0.65	3.81	0.86	0	0.27	4.36	11.8
5	0.64	3.22	0	0.34	0.11	5.37	15.4
6	0	16.7	2.70	4.00	0	0	0
7	0.22	3.59	ND	ND	ND	6.49	15.5
8	0	17.9	0	0	0	10.6	22.4
9	13.4	7.49	2.57	4.15	2.22	16.4	18.1
10	1.06	5.67	0	1.96	3.29	12.6	18.3
11	1.46	5.77	2.08	2.94	2.05	2.15	7.40
12	ND	ND	ND	ND	ND	ND	20.0
13	0	1.44	0	0	0	21.6	8.75
14	3.48	4.20	ND	ND	ND	8.77	12.2
15	0	4.65	0.88	0.82	0	7.90	18.8
16	0	2.94	0	0.33	0.45	6.49	9.17
17	0.82	11.2	4.38	8.93	5.41	16.1	47.8
18	4.03	5.07	2.42	0	0.35	10.9	16.3
19	0.37	2.30	0	0	0	5.83	8.00
20	4.10	3.21	<0.40	0.68	<0.30	7.68	17.9

[a] Analytes: B = benzene; CB = chlorobenzene;
1,2-DCB = 1,2-dichlorobenzene;
1,3-DCB = 1,3-dichlorobenzene;
1,4-DCB = 1,4-dichlorobenzene;
EB = ethylbenzene; and T = toluene.

[b] ND = not detected.

[c] < = less than.

APPENDIX F

REVISED DATA FROM LABORATORY 12

TABLE 45. REVISED DATA FROM LABORATORY 12
(µg/L)

Water matrix	Ampul	Benzene	Chlorobenzene	1,2-DCB	1,3-DCB	1,4-DCB	Ethylbenzene	Toluene
Distilled water	1	ND	2.97	12.3	5.41	4.27	2.44	2.64
	2	ND	2.37	12.3	6.76	6.10	2.23	1.92
	3	40.0	43.0	43.5	47.8	38.8	30.0	34.3
	4	100	45.5	42.5	50.2	41.3	33.3	45.0
	5	375	495	339	451	338	351	432
	6	344	465	339	434	338	334	420
Tap water	1	1.30	2.97	5.48	4.06	4.27	3.60	2.76
	2	0	3.66	5.48	4.06	4.27	3.90	3.12
	3	34.5	40.0	48.0	42.3	50.3	41.3	38.5
	4	50.0	46.5	45.3	55.5	45.0	49.5	44.5
	5	594	475	I	417	313	509	450
	6	375	599	424	543	427	657	564
Surface water	1	ND	3.25	0.75	1.25	1.25	2.50	2.25
	2	0.75	4.25	0.75	1.50	1.63	3.25	3.25
	3	42.3	45.8	63.5	45.0	46.3	61.0	38.8
	4	76.3	49.0	36.3	79.5	67.5	53.3	51.3
	5	500	792	396	503	388	627	637
	6	438	817	480	607	463	642	618

(continued)

TABLE 45 (continued)
(μg/L)

Water matrix	Ampul	Benzene	Chlorobenzene	1,2-DCB	1,3-DCB	1,4-DCB	Ethylbenzene	Toluene
Wastewater 1	1	0	0 (20.3)[a]	2.74	0	0	5.49	0 (18.0)
	2	0	0	5.48	0	0	7.93	0
	3	37.5	63.8	53.5	72.8	59.3	70.0	42.5
	4	47.0	70.8	59.3	86.8	57.5	52.3	54.0
	5	344	515	396	521	375	522	450
	6	469	619	452	608	450	674	510
Wastewater 2	1	5.2	1.41 (144)	4.11	2.70	3.05	5.31	13.5 (91.2)
	2	ND	4.34	5.33	4.43	5.12	2.33	4.81
	3	47.0	72.5	70.5	78.0	60.0	67.8	40.5
	4	90.8	61.8	33.8	43.3	33.8	65.8	32.8
	5	375	728	367	469	363	539	582
	6	244	743	424	573	438	531	558
Wastewater 3	1	0	1.44	1.03	0	0	2.50	4.20 (20.0)
	2	0	1.59	1.37	1.69	1.25	2.65	3.65
	3	26.0	34.5	48.0	52.0	41.3	47.3	30.0
	4	110	35.3	34.0	41.5	33.8	49.3	54.0
	5	347	491	368	486	375	538	468
	6	I	569	I	625	475	627	486

NOTE: 1,2-DCB = 1,2-Dichlorobenzene; 1,3-DCB = 1,3-Dichlorobenzene; 1,4-DCB = 1,4-Diclorobenzene; ND = not detected; I = eligible.

[a] Values in parentheses are blank values.

APPENDIX G

EFFECTS OF WATER TYPE ON PRECISION AND ACCURACY

TABLE 46. EFFECT OF WATER TYPE ON BENZENE ANALYSIS

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                         ** POINT ESTIMATES **

          DISTILLED WATER SLOPE:GAMMA(1) =  .96259

          WATER    INTERCEPT(WATER-DISTILLED)  SLOPE(WATER-DISTILLED)

            2                .1009                    -.0082
            3               -.0162                     .0090
            4               -.3490                     .0636
            5               -.3257                     .0502
            6               -.0628                     .0122


                        ** ANALYSIS OF VARIANCE **

              SOURCE          DF   SUM OF SQUARES  MEAN SQUARE     F     PROB

          REG(DISTILLED)        1    2714.78106    2714.78106
          REG(WATER/DISTILLED) 10       5.16795        .51680    3.87   .0000
          ERROR               578      77.12518        .13343

          TOTAL               589    2797.07419


** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

                    INTERCEPT(WATER-DISTILLED)            SLOPE(WATER-DISTILLED)
          WATER     ESTIMATE       INTERVAL              ESTIMATE       INTERVAL

            2         .1009  ( -.1841 ,   .3859)       -.0082  ( -.0740 ,   .0576)
            3        -.0162  ( -.3094 ,   .2770)        .0090  ( -.0583 ,   .0763)
            4        -.3490  ( -.6331 ,  -.0649)        .0636  ( -.0019 ,   .1290)
            5        -.3257  ( -.6201 ,  -.0314)        .0502  ( -.0171 ,   .1174)
            6        -.0628  ( -.3601 ,   .2345)        .0122  ( -.0559 ,   .0802)
```

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 47. EFFECT OF WATER TYPE ON CHLOROBENZENE ANALYSIS

```
                          ** POINT ESTIMATES **

          DISTILLED WATER SLOPE:GAMMA(1) = 1.00365

          WATER    INTERCEPT(WATER-DISTILLED)   SLOPE(WATER-DISTILLED)

            2               .0583
            3             -.0962                        -.0136
            4               .1265                         .0079
            5              1.2507                        -.0324
            6             -.0863                         -.2547
                                                          .0109


                         ** ANALYSIS OF VARIANCE **

              SOURCE              DF   SUM OF SQUARES  MEAN SQUARE    F     PROB

          REG(DISTILLED)           1    2433.11595     2433.11595
          REG(WATER/DISTILLED)    10      16.39476        1.63948   10.03  .0000
          ERROR                  556      90.91787         .16352

          TOTAL                  567    2540.42858


    ** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

                        INTERCEPT(WATER-DISTILLED)              SLOPE(WATER-DISTILLED)
          WATER        ESTIMATE      INTERVAL                 ESTIMATE      INTERVAL

            2             .0583  ( -.2586 ,    .3751)     -.0136  ( -.0873 ,   .0601)
            3           -.0962  ( -.4096 ,    .2171)       .0079  ( -.0646 ,   .0803)
            4             .1265  ( -.2253 ,    .4783)     -.0324  ( -.1115 ,   .0466)
            5            1.2507  (   .8375 ,  1.6639)     -.2547  ( -.3430 ,  -.1663)
            6           -.0863  ( -.4049 ,    .2322)       .0109  ( -.0626 ,   .0844)

NOTE:  IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN
       DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

       THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION
       AND ACCURACY REGRESSIONS PERFORMED EARLIER.
```

TABLE 48. EFFECT OF WATER TYPE ON 1,2-DICHLOROBENZENE ANALYSIS

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                         ** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) =  .96849

WATER    INTERCEPT(WATER-DISTILLED)   SLOPE(WATER-DISTILLED)

  2               -.0125                      -.0006
  3               -.0544                       .0036
  4               -.0133                      -.0065
  5               -.0944                       .0194
  6               -.5270                       .0929


                       ** ANALYSIS OF VARIANCE **

      SOURCE              DF   SUM OF SQUARES  MEAN SQUARE    F     PROB

REG(DISTILLED)             1    2526.32257     2526.32257
REG(WATER/DISTILLED)      10       4.80336        .48034     4.41  .0000
ERROR                    553      60.22882        .10891

TOTAL                    564    2591.35476
```

```
** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

              INTERCEPT(WATER-DISTILLED)             SLOPE(WATER-DISTILLED)
WATER       ESTIMATE       INTERVAL               ESTIMATE        INTERVAL

  2          -.0125  (  -.2783 ,   .2532)        -.0006  (  -.0610 ,   .0599)
  3          -.0544  (  -.3337 ,   .2249)         .0036  (  -.0594 ,   .0666)
  4          -.0133  (  -.2857 ,   .2591)        -.0065  (  -.0678 ,   .0549)
  5          -.0944  (  -.3704 ,   .1816)         .0194  (  -.0429 ,   .0816)
  6          -.5270  (  -.8023 ,  -.2516)         .0929  (   .0305 ,   .1554)
```

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 49. EFFECT OF WATER TYPE ON 1,3-DICHLOROBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = 1.00172

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0835	-.0202
3	.0393	-.0118
4	.6491	-.1319
5	-.0031	-.0049
6	.0376	-.0094

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	2438.20602	2438.20602		
REG(WATER/DISTILLED)	10	4.85398	.48540	4.61	.0000
ERROR	558	58.80602	.10539		
TOTAL	569	2501.86602			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	.0835	(-.1811 , .3480)	-.0202	(-.0810 , .0407)
3	.0393	(-.2166 , .2953)	-.0118	(-.0709 , .0472)
4	.6491	(.3416 , .9565)	-.1319	(-.1991 , -.0647)
5	-.0031	(-.2809 , .2747)	-.0049	(-.0672 , .0574)
6	.0376	(-.2279 , .3032)	-.0094	(-.0701 , .0513)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 50. EFFECT OF WATER TYPE ON 1,4-DICHLOROBENZENE ANALYSIS

```
                         ** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = 1.02156

WATER    INTERCEPT(WATER-DISTILLED)   SLOPE(WATER-DISTILLED)

  2              .2074                       -.0441
  3              .1052                       -.0299
  4              .2237                       -.0513
  5              .2613                       -.0479
  6              .1215                       -.0255


                        ** ANALYSIS OF VARIANCE **

      SOURCE               DF   SUM OF SQUARES  MEAN SQUARE    F     PROB

REG(DISTILLED)              1    2562.10267     2562.10267
REG(WATER/DISTILLED)       10       1.27788        .12779     1.49  .1378
ERROR                     569      48.68753        .08557


TOTAL                     580    2612.06809


** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

                INTERCEPT(WATER-DISTILLED)            SLOPE(WATER-DISTILLED)
    WATER       ESTIMATE       INTERVAL               ESTIMATE       INTERVAL

      2           .2074  (  -.0275 ,    .4424)       -.0441  (  -.0979 ,    .0098)
      3           .1052  (  -.1224 ,    .3327)       -.0299  (  -.0823 ,    .0225)
      4           .2237  (  -.0340 ,    .4813)       -.0513  (  -.1086 ,    .0059)
      5           .2613  (   .0166 ,    .5059)       -.0479  (  -.1030 ,    .0071)
      6           .1215  (  -.1174 ,    .3603)       -.0255  (  -.0799 ,    .0289)
```

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 51. EFFECT OF WATER TYPE ON ETHYLBENZENE ANALYSIS

** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) = .97585

WATER	INTERCEPT(WATER-DISTILLED)	SLOPE(WATER-DISTILLED)
2	.0594	-.0021
3	-.0331	.0074
4	.0187	-.0017
5	-.2306	.0338
6	.0276	.0004

** ANALYSIS OF VARIANCE **

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB
REG(DISTILLED)	1	2642.15194	2642.15194		
REG(WATER/DISTILLED)	10	1.88110	.18811	1.83	.0532
ERROR	578	59.52390	.10298		
TOTAL	589	2703.55693			

** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

WATER	INTERCEPT(WATER-DISTILLED) ESTIMATE	INTERCEPT(WATER-DISTILLED) INTERVAL	SLOPE(WATER-DISTILLED) ESTIMATE	SLOPE(WATER-DISTILLED) INTERVAL
2	.0594	(-.1974 , .3162)	-.0021	(-.0610 , .0569)
3	-.0331	(-.2934 , .2271)	.0074	(-.0524 , .0672)
4	.0187	(-.2357 , .2732)	-.0017	(-.0607 , .0573)
5	-.2306	(-.4870 , .0258)	.0338	(-.0251 , .0927)
6	.0276	(-.2362 , .2914)	.0004	(-.0597 , .0604)

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.

TABLE 52. EFFECT OF WATER TYPE ON TOLUENE ANALYSIS

```
                      ** POINT ESTIMATES **

DISTILLED WATER SLOPE:GAMMA(1) =  .97114

WATER    INTERCEPT(WATER-DISTILLED)   SLOPE(WATER-DISTILLED)

  2                -.0797                     .0107
  3                -.2191                     .0358
  4                 .0196                    -.0208
  5                 .6483                    -.1273
  6                -.0574                     .0058


                    ** ANALYSIS OF VARIANCE **

     SOURCE            DF   SUM OF SQUARES  MEAN SQUARE    F     PROB

REG(DISTILLED)          1    2486.53914     2486.53914
REG(WATER/DISTILLED)   10       7.11968         .71197    5.13  .0000
ERROR                 565      78.42011         .13880


TOTAL                 576    2572.07893



** TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES **

              INTERCEPT(WATER-DISTILLED)           SLOPE(WATER-DISTILLED)
WATER         ESTIMATE        INTERVAL             ESTIMATE         INTERVAL

  2           -.0797  (  -.3705 ,    .2110)      .0107  (  -.0568 ,    .0782)
  3           -.2191  (  -.5072 ,    .0689)      .0358  (  -.0311 ;    .1026)
  4            .0196  (  -.2740 ,    .3132)     -.0208  (  -.0882 ,    .0466)
  5            .6483  (   .2932 ,   1.0034)     -.1273  (  -.2046 ,   -.0500)
  6           -.0574  (  -.3580 ,    .2431)      .0058  (  -.0629 ,    .0744)
```

NOTE: IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN DISTILLED WATER AND THE CORRESPONDING WASTE WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.